01 Feb 2002

Studies on Use of Carbon Slurry, A Waste from Fertilizer Plant, in Treatment of Waste Water

Sanjay Tewari

STUDIES ON USE OF CARBON SLURRY, A WASTE FROM FERTILIZER PLANT, IN TREATMENT OF WASTE WATER

A DISSERTATION

Submitted in partial fulfilment of the requirements for the award of the degree of

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

SANJAY TEWARI

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667 (INDIA)

FEBRUARY, 2002

CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled "**STUDIES ON USE OF CARBON SLURRY, A WASTE FROM FERTILIZER PLANT, IN TREATMENT OF WASTE WATER**", in partial fulfillment of the requirement for the award of the degree of Master of Technology in Chemical Engineering with specialization in **Industrial Pollution Abatement**, submitted in the Department of Chemical Engineering, Indian Institute of Technology-Roorkee, Roorkee, is an authentic record of my own work carried out during the period from July 2001 to January 2002, under the supervision of **Dr. I. D. Mall**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology, Roorkee.

The matter embodied in this dissertation has not been submitted for the award of any other degree.

Date : Feb, 28th, 2002 **(SANJAY TEWARI)**

Place : Roorkee

CERTIFICATE

This is certified that the above statement made by the candidate is correct to the best of my knowledge.

(I. D. MALL)
Associate Professor,
Deptt of Chemical Engg.
Indian Institute of Technology
Roorkee -247667
India

ACKNOWLEDGEMENT

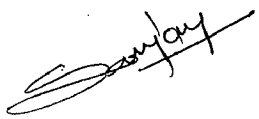
I express my deep sense of gratitude to my guide **Dr. I. D. Mall**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology - Roorkee, Roorkee, for his keen interest, constant guidance and encouragement throughout the course of this work. His experience, assiduity and deep insight of the subject held this work always on smooth and steady course. Useful criticism and personal help extended in the hour of need had been immensely useful.

Thanks are due to Dr. I. M. Mishra, Professor and Head, Department of Chemical Engineering, Indian Institute of Technology - Roorkee, Roorkee, for providing various facilities during this dissertation.

I am highly thankful to Shri B. K. Arora (SLT, PAR Lab), Shri Bhag Singh (SLT, MTR Lab), Shri Ayodhya Prasad, Shri Satyapal Singh, Mrs. Rekha Sharma and Mr. Jawal Singh for their continuous help provided during experimental work.

I am greatly indebted to Nripendra, Narayana, Sushil, Sachin, Mahendra, Dhananjay, and Aneesha for their help in the experimental work.

Last but not the least, it is all owed to the blessings of my parents and God that I have come up with this work in due time.



(SANJAY TEWARI)

ABSTRACT

Non biodegradable materials like heavy metals, refractory organics are not removed during the conventional treatment process. In order to meet the regulatory standards and for safe disposal, it is necessary to go for tertiary treatment. Various tertiary treatment methods include adsorption, membrane separation process, ultra filtration, reverse osmosis etc. Adsorption has been found to be efficient for the removal of most of heavy metals in waste water at lower concentrations. Activated carbon is commonly used adsorbents, however, due to its high cost and loss in regeneration, various low cost adsorbents have been investigated during recent years.

The aim of the present work is to explore the possibility of utilizing carbon slurry, which is produced during partial oxidation of hydrocarbons,for the treatment of industrial waste water. In the present work carbon slurry has been used for the treatment of heavy metals like Cr(vi), Ni(ii), Zn(ii) which are present in fertilizer plant waste water. Carbon slurry has also been used for treatment of three industrial waste effluents from phenol formaldehyde resin, polyester plant and sugar industry.

Proximate analysis, chemical analysis, particle size analysis, surface area determination, XRD and SEM studies were conducted for characterizing the carbon slurry. Batch studies were conducted to see the effect of contact time, adsorbent dose and initial concentration on removal of Cr(vi),Ni(ii) and Zn(ii). Equilibrium data were fitted in Langmuir and Freundlich isotherms. Removal to the extent of 90% was achieved for Cr(VI), and 85% for Ni(II) and

Zn(II) using carbon slurry as adsorbent. Hence carbon slurry has good adsorptive capacity for Cr(vi), Ni(ii) and Zn(ii).Kinetics of removal has also been presented, which shows that removal follows first order kinetics. Weber and Morris plot show that intra particle diffusion is the rate controlling step.

Some studies on the competitive adsorption of heavy metals (Cr(vi),Ni(II) and Zn(II)) in multi cationic solutions have been carried out.It is found that chromium is readily adsorbed in comparison to nickel and zinc in a waste water containing all three. Experiments were carried out for the removal of COD of waste water from polyester industry waste, phenol formaldehyde resin plant and sugar mill effluent and results show that carbon slurry is suitable substitute for activated carbon. Adsorption of Cr, Ni, Zn was found in the order Cr>Zn>Ni.

NOMENCLATURE

C_o	Initial concentration of effluent
C_{Ab}	Desired concentration of adsorbate at break through, (mg l^{-1})
C_e	Concentration of adsorbate solution at equilibrium, (mg l^{-1})
K	Adsorption rate constant, (min^{-1})
k	Intra-particle diffusion rate constant, (mg g^{-1} $min^{-0.5}$)
K_a	Rate constant, l liquid / mg of adsorbent, (l mg^{-1})
K_A	Langmuir isotherm constant, (l mg^{-1})
K_F	Freundlich isotherm constant, (mg l^{-1}) $^{-1/n}$
n	Freundlich isotherm constant
q	Amount of adsorbate adsorbed per unit amount of adsorbent at time t, (mg g^{-1})
q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg g^{-1})
q_m	Limiting adsorbing capacity, (mg g^{-1})

LIST OF FIGURES

LIST OF TABLES

CONTENTS

Chapter 1

INTRODUCTION

1.1 GENERAL

Environmental degradation has become one of the major concern during recent years due to industrial and unplanned urbanization. It has been increasingly noticeable, the growing awareness of public in general and particularly of enterpreneurs, concerning the condition that have a negative impact over the environment, water quality being one of their main consideration. The deterioration of water quality started with industrialization and worsened with, owing to expansion of industry, growing scarcity of water resources and ever increasing demand for domestic and industrial processes. Untreated discharges from industrial activities and urban agglomerates into water bodies are the main sources of both punitively and qualitatively.

Sources of water are limited and, therefore, treatment and reuse of utilized wastewater seems to be the ultimate solution to the problem. In that order, choice of a particular treatment process should be made with appropriate consideration of available capital and operating cost, land requirement and other specific needs of the process. The various wastewater treatment techniques include primary treatment like screening, grit removal, primary sedimentation, floatation and flow equalization, secondary treatment, like biological treatment, activated sludge process and then finally tertiary treatment which include adsorption, membrane separation, ultrafiltration, reverse osmosis, coagulation and precipitation, biological treatment using special microbes, etc. Industrial effluents may contain acids, alkalies,

undesirable chlorides, phenols, sulphates, etc. and salts of metals such as iron, mercury, lead, chromium, cadmium, nickel, magnesium, manganese, etc. Precipitation of pollution species as sulfides, hydroxides, etc., is the most common method used for their removal from waste water. But major problem associated with this type of treatment is sludge disposal. Ion exchange as a tool of wastewater treatment has also been reported. Though, it does not pose a significant sludge disposal problem, it is an expensive treatment technique. Moreover, this technique is not selective for a variety of species and has the disadvantage of having a rather critical flow rate necessary for efficient removal.

Adsorption is well organised as a unit operation for the removal of pollutants present in trace amount in wastewater which otherwise cannot be removed efficiently by other conventional methods. Almost complete removal of impurities with negligible side effects explains its wide applications in tertiary treatment and pollution stages. Large number of adsorbents are available which can be utilised for the removal of heavy metals. Use of activated carbon for wastewater renovation has been popular in more advanced countries, but high cost limits its application to the developing countries. Moreover, about 10 to 15% of its mass is lost during conventional regeneration process. It has also been observed that the regenerated carbon has a comparatively lower adsorption capacity. Due to this discrepancy with activated carbon, search for an alternative continues. Therefore, the prospects of a number of waste materials as substitutes for the otherwise costly activated carbon for the wastewater treatment has been investigated extensively. Recently, low cost materials have received considerable attention for use as adsorbents like caol fly ash, bottom ash, bagasse fly ash, peat, wood, carbon slurry, sunflower stalks, peat mass, modified coal, etc. for

removal of organic refractories, heavy metal, colour, dyes, etc. A critical review of this has been presented by Mall et al. (1996) and Bailey et al (1998). Main objective of the various researchers have been to provide a potentially viable substitute for activated carbon.

Here the use of carbon slurry is investigated in treatment of industrial waste water as a substitute for expensive activated carbon. About 1.45 kg carbon slurry per ton of ammonia is produced. Carbon slurry is dumped as waste in fertilizer plants. However, looking at the characteristics of the carbon slurry, there is wide scope for using it as adsorbent. Some work has been done on activated carbon for removal of organic compounds, heavy metals, colour, dyes, etc. in synthetic wastewater. However, no work has been done for its application for treatment of actual waste. No work has been done for use of carbon slurry for treatment of industrial waste. In the present work, carbon slurry has been used for treatment of industrial wastes, like polyester industry effluents and phenol formaldehyde resin plant effluents. Heavy metals like chromium, nickel, arsenic are present in fertilizer plant waste. A special attention has been paid to the studies for removal of these metals from wastewater in the present work.

1.2 CARBON SLURRY

In India, ammonia plants of fertilizer industry, operating on the process of partial oxidation of hydrocarbons generate fine carbon particles, which when scrubbed from gas stream produce aqueous carbon slurry (CS) containing 2-3% carbon. It is estimated that production of carbon slurry is about 1.45 kg/tonne ammonia produced. This slurry creates disposal problem. It is a very efficient non-conventional adsorbent having adsorptive surface area in the range of 300-400 m^2/g. Efforts have been made to convert this

slurry into a dried carbon slurry from National Fertilizer Ltd. (NFL), Panipat, India has collected and is used without any pretreatment.

1.3 TYPICAL EFFLUENTS FROM INDUSTRIES

Industries are producing tremendous amount of waste round the clock all through the years. The industrial waste may be degradable, non-degradable (conservative) and biologically accumulative (persistent). This waste is creating problem and is of varied nature thereby creating problem in treating them before discharge. This ultimately leads to an increase in treatment cost. Present work deals with waste from effluents from phenol, polyester and sugar industry and synthetic waste for heavy metals containing Cr(VI), Ni(II) and Zn(II). These metals are present predominantly in wastewater from fertilizer industry and electroplating industry and are of hazardous nature. The wastes from these industries have significantly high COD. Some experiments were carried out for studying the effect of adsorption using carbon slurry as adsorbents on chemical oxygen demand (COD) of wastewater.

1.4 OBJECTIVES OF PRESENT STUDY

Present study has been taken with objective to investigate the suitability of utilization of carbon slurry, a waste from fertilizer plants, as adsorbent for the treatment of industrial wastewater, for removal of non-biodegradable materials and trace metals. Various parameters affecting adsorption were presented. Kinetics of removal and adsorption isotherm data for evaluation of adsorption capacity were presented.

The experimental work consists of

- Characterization of adsorbent
  - Proximate analysis

- Chemical analysis
- X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) studies
- Particle size analysis

- Characterization of industrial wastewater
  - Characterization of wastewater from phenol formaldehyde plants
  - Characterization of wastewater from polyester industry
  - Characterization of wastewater from sugar mills

    Various parameters like pH, turbidity, total solids, dissolved solids and suspended solids, dissolved oxygen (DO), COD, BOD_5, oil and grease, chlorides and phenols are determined for these wastes.
- Batch experiments to study
  - The effect of initial concentration
  - The effect of contact time
  - The effect of adsorbent dose
  - Equilibrium studies for adsorption equilibrium isotherm (Freundlich and Langmuir)
  - Competitive adsorption of Cr(V)), Ni(II) and Zn(II), for multi cationic solution.
  - Kinetics of removal
- Effect of adsorption by carbon slurry on COD of different industrial wastes.

Chapter 2

CARBON SLURRY: A WASTE FROM FERTILIZER PLANT

2.1 GENERAL

In this investigation we have used carbon slurry, a waste from fertilizer plant as an adsorbent for the removal of heavy metals viz. Cr(VI), Ni(II) and Zn(II). Present chapter lines complete details regarding the process generation of carbon slurry from fertilizer plants.

2.2 GENERATION OF CARBON SLURRY FROM FERTILIZER PLANT

Carbon slurry is a waste product generated during partial oxidation of hydrocarbons during manufacturing of ammonia. In fertilizer plants during partial oxidation of heavy fuel oils, the fine carbon particles produced in the reaction are scrubbed from the gas stream and aqueous carbon slurry (CS) containing 2-3 percent carbon is produced. It is estimated that production of CS is about 1.45 kg per tonne of ammonia produced. It is a very efficient non-conventional adsorbent having adsorptive surface area in the range of 300-400 m^2/g.

As an alternative use this carbon can be processed with oil and carbon- oil slurry can be returned to the gasification reactor along with other fuel or burned in a boiler. Other process of separating carbon may be either by pelleting or by the use of specially designed continuously operating vacuum filters in the latter, carbon is recovered in commercially usable form. This process also recovers water, which is used again in making carbon slurry. Efforts have been made to convert the waste slurry into a cheap

carbonaceous adsorbent material **(Srivastava et al., 1989)**. Here naturally dried carbon slurry from National Fertilizer Limited (NFL), Panipat, India was collected and is used without any pretreatment.

2.2.1 Thermal Decomposition

The thermal decomposition of hydrocarbons appears as a side reaction in the processes of controlled oxidation with oxygen and water reforming, the only ones commercialized at present. Many different feed stocks are employed: natural gas (methane, ethane, propane etc.), petroleum cuts (Liquefied Petroleum Gas: LPG, naphtha, fuel oil, vacuum residues, asphalt etc.).

Depending on the specific case (catalytic or other process), the previous removal of certain impurities may or may not be necessary: sulfur derivatives. Mercury, other metals. Furthermore, they yield effluents of variable compositions, which must be treated to improve the total yield of the operation. Figure 2.1 provides a glance of the succession of treatment which accompanies the two basic industrial processes used for the manufacture of hydrogen:

(a) Partial oxidation.

(b) Steam reforming.

The following operations are carried out:

(a) Conversion of CO with steam (shift conversion).

(b) Extraction of acid gases CO_2 and H_2S, supplemented in the case of sulfur containing effluents by different units designed to prevent pollutant release in to the atmosphere.

(c) Final purification designed to eliminate the last farces of CO.

Depending on the flow sheet concerned, the pretreatment comprise:

(a) For steam reforming: desulphurization essentially intended to protect the catalyst.

(b) For partial oxidation with oxygen: air distillation.

2.2.2 Partial Oxidation

This type of process can theoretically be used to treat any gaseous, liquid or solid feed. In practice, however, it is reserved for the conversion of cheapest raw materials such as heavy hydrocarbons (especially fuel oil), and possibly, petroleum residues (asphalt), coal and biomass (wood). In this case, moreover, the conversion is usually called "gasification"

2.2.3 Thermodynamic and kinetic aspects of the reaction.

The chemical mechanism involved in the controlled oxidation of hydrocarbons is extremely complex. a simplified interpretation can nevertheless be provided by considering methane. The following transformations are considered in this case:

(a) Combustion reaction: since it takes place at elevated temperature, at which carbon monoxide is one of the main products formed, it is convenient for thermodynamics calculations to assume the following overall representation due to the presence of water formed during combustion or added by steam injection

$$CH_4 + 3/2\ O_2 \longrightarrow CO + 2\ H_2O$$

(b) For carbon monoxide, the following equilibrium must be added:

$$CO + H_2O \rightleftharpoons CO_2 + H_2O$$

.A hydro carbon decomposition reaction:

$$CH_4 \rightleftharpoons C(g) + 2H2$$

The first conversion is exothermic and exentropic: it is virtually complete and also serves to reach the temperature required for the operation, with the exception of preheating at allow temperature level, takes place adiabatically. The second reaction depends on an equilibrium, which shifts in the desired direction at low temperature. From a thermodynamic point of view, to obtain high hydrogen contents in the effluents produced (raw synthesis gas), the operating conditions must guarantee the lowest possible service temperature. In practice, this consideration is incompatible with the partial oxidation operation, which, due to its exothermicity, creates a high reaction temperature (950 to 1250).

This effect must therefore be corrected by a supplementary catalytic conversion of CO, after having cooled the gas obtained. Thus, by excess water injection and by lowering the temperature, the conditions reached cause the equilibrium to shift the production of hydrogen.

The third conversion, the decomposition of methane into its elements, favored by the high temperature, is the main side reaction. To a certain degree, the presence of CO_2 and water helps to offset these harmful effects, due to the formation of powdery carbon, by means of the following equilibrium:

$$CO_2 + C \rightleftharpoons 2CO$$

$$C + H_2O \rightleftharpoons CO + H_2$$

Available literatures show that avoiding the production of carbon black can yield a low methane content in the final gas, which can be adopted by adjusting the initial O_2/ CH_4 ratio.

In the case of heavier hydrocarbons the basic conversion is the following:

$$C_nH_m + \frac{(2n+m)}{4} O_2 \rightleftharpoons n\,CO + (m/2)\,H_2O$$

As the H/C ratio in the field decreases, the tendency to favor the production of carbon increases. Since the amount of water formed from by combustion becomes insufficient, it is therefore necessary to operate in the presence of steam, even at elevated temperature. Thermodynamic calculation shows that, at identical temperatures an increase in pressure results in larger water requirements and a decrease in oxygen requirement. Simultaneously, the residual methane content increases, and raising the temperature can offset this Highest carbon content feedstock (residues, coal, and biomass) constitutes the limit case.

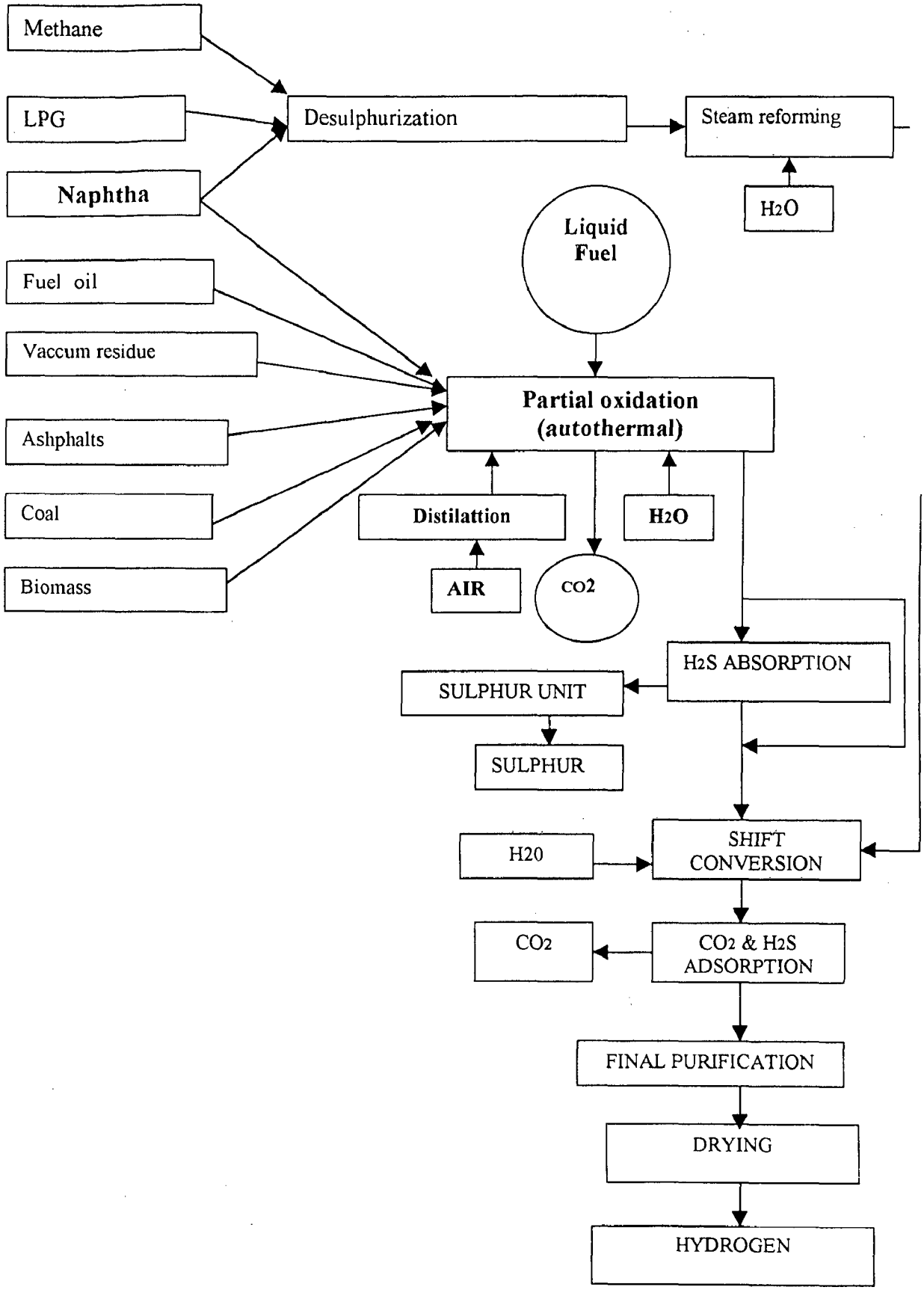


Fig. 2.1 Processing of carbanous feedstock to produce hydrogen

Chapter 3

INDUSTRIAL WASTE: FERTILIZER PLANT, POLYESTER PLANT, PHENOL-FORMALDEHYDE PLANT AND SUGAR PLANT

3.1 GENERAL:

Mass industrialization, in its wake brings large quantities of industrial wastes, which find their way into either the air or natural water bodies, there by posing menacing problems for the mankind. Present chapter gives in detail about, the waste generated by

- Fertilizer Industry
- Sugar Industry
- Phenol-Formaldehyde Industry, and
- Polyester Plant

Further, details regarding sources of heavy metals in the industrial waste water are also given.

The chapter also comprises of relevant environmental standards, MINAS, or various effluents and their adverse effects on human being.

3.2 FERTILIZER INDUSTRY

Due to production of fertilizer at vary large scale, this industry is very much critical with respect to the environmental considerations. The characteristics of the wastewater from nitrogenous fertilizer plants are shown in Table 3.1.The major pollutants in the wastewater are ammonia, urea, carbon slurry, arsenic, chromium and oil. The urea is not toxic to fish and aquatic life, but its bacterial decomposition changes it into ammonia.

Ammonia is the most toxic to the fish, can be converted to nitrates to deplete oxygen resources and lead to eutrofication of water bodies, if the wastewater is directly discharged. Several methods are available for the treatment ammonia bearing waste e.g.,

(i) Steam stripping,

(ii) Air stripping ,

(iii) Lagooning after pH adjustment,

(iv) Cultivation of protein rich algae by utilizing the nitrogenous effluents]

(v) Biological nitrification and denitrification.

But neither of them is as efficient as adsorption for removal of chromium, ammonia, arsenic etc.

TABLE 3.1: Effluents standards for the fertilizer industry

(Straight-Nitrogenous Fertilizers excluding the Calcium, Ammonium Nitrate and Ammonium Nitrate Fertilizer.)

		Plant Commissioned after 1.1.82	before 1.1.82
pH		6.5-8.0	6.5-8.0
Ammonical Nitrogen	mg/l	50	75
Total Kjeldhal Nitrogen	mg/l	100	150
Free Ammonical Nitrogen	mg/l	4	4
Nitrate Nitrogen	mg/l	10	10
Cyanide (as CN)	mg/l	0.2	0.2
Vanadium (as V)	mg/l	0.2	0.2
Arsenic (as As)	mg/l	0.2	0.2
Suspended Solids	mg/l	100	100
Oil and Grease	mg/l	10	10
*Hexavalent Chromium (as Cr^{+6})	mg/l	0.1	0.1
**Total Chromium (as Cr)	mg/l	2.0	2.0

Straight Nitrogenous Fertilizers including the Calcium, Ammonium Nitrate and Ammonium Nitrate Fertilizer.

		Plant Commissioned after 1.1.83	before 1.1.82
pH		6.5-8.0	6.5-8.0
Ammonical Nitrogen	mg/l	50	75
Total Kjeldhal Nitrogen	mg/l	100	150
Free Ammonical Nitrogen	mg/l	4	4
Nitrate Nitrogen	mg/l	20	20
Cyanide (as CN)	mg/l	0.2	0.2
Vanadium (as V)	mg/l	0.2	0.2
Arsenic (as As)	mg/l	0.2	0.2
Suspended Solids	mg/l	100	100
Oil and Grease	mg/l	10	10
*Hexavalent Chromium (as Cr^{+6})	mg/l	0.1	0.1
**Total Chromium (as Cr)	mg/l	2.0	2.0

Straight Nitrogenous Fertilizers excluding the Calcium, Ammonium Nitrate and Ammonium Nitrate Fertilizer.

		Plant Commissioned after 1.1.84	before 1.1.82
pH		6.5-8.0	6.5-8.0
Ammonical Nitrogen	mg/l	50	75
Total Kjeldhal Nitrogen	mg/l	100	150
Free Ammonical Nitrogen	mg/l	4	4
Nitrate Nitrogen	mg/l	10	10
Cyanide (as CN)	mg/l	0.2	0.2
Vanadium (as V)	mg/l	0.2	0.2
Arsenic (as As)	mg/l	0.2	0.2
Phosphate (as P)	mg/l	5	5
Suspended Solids	mg/l	100	100
Oil and Grease	mg/l	10	10
*Hexavalent Chromium (as Cr^{+6})	mg/l	0.1	0.1
**Total Chromium (as Cr)	mg/l	2.0	2.0

**To be complied with at the outlet of fluoride removal unit. If the recipient system so demands, fluoride as F shall be limited to 1.5 mg/l.*

***To be complied with at the outlet of chromate removal unit.*

3.3 SUGAR INDUSTRY WASTE

1-5 tonnes of water/tonne of sugar is utilized in different operations, but varies from industry to industry and even operation to operation. An appreciable fraction of water is consumed in extraction operations. The other operations are filter washing, boiler house operations, crystal washing and heat exchangers. The sources of pollution are leakage, spill-overs, overloading and indifferent handling during crushing and extraction operations, pumping, evaporation, crystallization, molasses storage and handling, blow off operations as well as filter washings. Table 3.2 gives typical characteristics of combined effluent from sugar industry excluding condenser water, while Table 3.2 gives MINAS for it.

Table 3.2 : characteristics of combined effluents of sugar industry

Sr. No.	Property	Concentartion
1	pH	4.6-7.1
2	Solids: (a) Total, mg/l (b) Suspended, mg/l (c) Volatile, mg/l	 870-3500 220-800 400-2000
3	BOD_5, 20°C, mg/l	300-2000
4	COD (dichromate method), mg/l	600-4380

3.4 PHENOL-FORMALDEHYDE INDUSTRY EFFLUENT

Phenol-formaldehyde resins constitute by far the largest proportion of a group of synthetic resins called Phenolic resins, probably the most varied and versatile resin we know. In the production process of two step resins the

phenol and formaldehyde are placed in the reaction kettle with the catalyst (sulphuric acid) and heated 3 to 4 hours at a temperature of 140 to 163° C. During condensation, reaction water is eliminated and forms the upper of the two layers. This water of the reaction is removed under vacuum without the addition of the heat. In the present study, this wastewater which is rich in chemical composition is taken for the treatment by carbon slurry.

3.4.1 Sources of Phenol and it Effects on Living Beings

Phenols defined as hydroxy derivatives of benzene and its condensed nuclei may occur in domestic and industrial wastewater, natural waste and potable water supplies. Phenols are among the most common water pollutants. Phenols may be present in raw water in owing to the discharge of wastewater from coke distillation plants, the petrochemical industry, plastics, rubber proofing, disinfectants, pharmaceuticals and numerous other industries where phenols serves as intermediates. Various researchers have found substantial amount of phenols in environment. Contaminated raw water including ground water may contain 1-10 mg of phenol and mono and di-chloro phenols per liter. Tri and tetrachlorophenols have been detected in raw water at levels of 1-10 mg/l and occasionally higher. Phenols can cause bad taste and odour in drinking water even at low concentration. A primary concern about the presence of phenols in wastewater is their toxic effect on aquatic life. Some phenolic compounds have found to accelerate tumor formation and to be ciliostatic (**Singh and Mishra, 1990**).

3.5 POLYESTER PLANT WASTE

The common polyester fibre are polymers of the ester formed from dimethyl terephthalate/TPA and ethylene glycol. Polymerization is a two-stage process in which the monomer is first prepared either by an ester interchange

between dimethyl terephthalate and ethylene glycol, or by direct esterification of terephthalic acid while the second stage is the polymerization of the monomer. The polymer is extruded from the bottom of the polymerizer though a slot or holes on to the surface of the surface of water cooled-drums. Acidic wastes is discharged after filtration from autoclave reactor. Table 3.3 gives MINAS for synthetic Fibre industries.

Table 3.3: MINAS for synthetic Fibre industries

Sr. No.	Parameter	Concentration not to exceed (mg/l except pH)
1	pH	5.5-9
2	Suspended solids	100
3	BOD_5	30
4	Zinc	1.0

3.6 SOURCES OF HEAVY METALS AND THEIR EFFECTS ON HUMAN BEINGS

Heavy metal contamination exists in aqueous waste streams of many process industries, metals plating facilities, mining operations and tanneries. The soils surrounding many military bases are also contaminated and poised a risk of metals groundwater and surface water contamination. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Among these, 'Minamata' tragedy due to mercury poisoning and 'Itai Itai' disease in Japan due to Cadmium toxicity and Arsenic pollution in West Bengal are well known. Here we are discussing only Cr(VI), Ni(II) and Zn(II) as they are found predominantly in fertilizer industry

waste. These metals ions are found in various industrial waste in significant quantity that's why they need special attention.

3.6.1 Sources of Chromium (VI) and its Effects on Human Beings

There are numerous sources of industrial effluents leading to chromium enrichment of the aquatic environment. Industrial wastewater including those from textile, leather tanning, electroplating, pigment and dyes, metallurgical and metal finishing contain chromium in high concentration.

Out of the two predominant forms of chromium, namely trivalent and hexavalent later is hazardous to biological activities. A number of health hazards due to chromium have been reported in the literature. These include malignant growth in respiratory tract, pain less perforation of nasal septum, causing ulcers in the mucous membrane, etc. The *maximum tolerance* of chromium has been fixed at *0.05 mg/l* and *0.1 mg/l* in the drinking (IS 10500-1983) and inland surface [IS 2490 (Part – I), 1970] water respectively.

3.6.2 Sources of Nickel(II) and its Effects on Human Beings

Typical soils contain large quantity of Nickel. Nickel is widely used in industry for its resistance to corrosion, high strength over a wide temperature range and good alloying properties. It is also used in metal plating for catalysts, for batteries and in certain fungicides.

Dermatitis is recognized to be the common symptom of industrial exposure to nickel, although high occupational exposures have been associated with renal problems and lung cancer. Women appear to be more sensitive than men by a factor of ten. High concentration of nickel can react with DNA, and can results damage in DNA. World Health Organization (WHO) has suggested that the maximum concentration of Nickel in drinking water should be 0.1 mg/l.

3.6.3 Sources of Zinc(II) and its Effects on Human Beings

Zinc is abundant element and constitutes approximately 0.04 g/kg of the earth's crust. The carbonates, oxides, and sulfides of zinc are sparingly soluble in water, while the highly soluble chloride and sulphate salts tend to form zinc hydroxide and zinc carbonate, as a result the concentration of zinc in natural water is generally low.

Symptoms of zinc toxicity in human include vomiting, dehydration, electrolyte imbalance and abdominal pain. Acute renal failure caused by zinc chloride has been reported. Zinc imparts to water an undesirable astringent taste, in addition water containing at concentration to excess of 5.0 mg/l may appear opalescent to develop a greasy film on boiling.

3.7 EFFLUENT STANDARDS

Table 3.4 presents effluent standards as given in Schedule VI of Environment (protection) Third Amendment Rules, 1993,Table 3.5 shows water requirement and characteristics of some selected industry wastes and Fig. 3.1 gives pictorial representation of some health and economic effects likely to result from discharge of solids, liquids and gaseous wastes into water.

Table 3.4: Effluent standards as given in Schedule VI of Environment (protection) Third Amendment Rules, 1993

S.N	Parameter	Standards			
		Inland surface water	Public sewers	Land for irrigation	Marine coastal areas
1	Colour and odor	See Footnote.	-	See Footnote.	See Footnote.
2	Suspended solids, mg/l	100	600	200	a) For process waste water 100 b) For cooling water effluent 10 % above total suspended matter of influent. c)

3	Particle size of suspended solids.	Shall pass 850 micron IS Sieve.			a) Floatable solids, max. 3mm b) Settleable solids max. 856 micron.
4	pH value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
5	Temperature	Shall not exceed 5^0C above receiving water temperature.	-	-	Shall not exceed 5^0C above receiving water temperature.
6	Oil & grease, mg/l	10	20	10	20
7	Total residual chlorine(mg/l)	1.0	-	-	1.0
8	Ammonical nitrogen as (N), mg/l	50	50	-	50
9	Free ammonia, mg/l	5.0	-	-	5.0
10	BOD_5 at 20°C, mg/l	30	350	100	100
11	COD, mg/l	250			250
12	Arsenic (as As), mg/l	0.2	0.2	0.2	0.2
13	Mercury (as Hg), mg/l	0.01	0.01	-	0.01
14	Lead (as Pb), mg/l	0.1	0.1	-	2.0
15	Cadmium (as Cd), mg/l	2.0	1.0	-	2.0
16	Chromium (VI), mg/l	0.1	2.0	-	1.0
17	Total chromium as Cr, mg/l	2.0	2.0	-	2.0
18	Zn, mg/l	5.0	15	-	15
19	Nickel, mg/l	3.0	3.0	-	5.0
20	Copper, mg/l	3.0	3.0	-	3.0
21	Phenolic compounds (C_6H_5OH), mg/l	1.0	5.0	-	5.0

- *These standards shall be applicable for industries, operations or processes other than those industries, operations or process for which standards have been specified in schedule I.*
- *All efforts should be made to remove colour and unpleasant odour as far practicable.*

Sr. No.	Industry	Wastewater characteristics			Nature of pollutants and characteristic effects
		Quantity	BOD_5	others	
1	Polyester	67-133 liter/kg of goods		200 kg/ 1000 kg of goods	
2	Fertilizers	***Per ton of NH_3:*** Carbon slurry, 2500 liter. Scrubber, 100-800 liter. NH_3 plant,2000-7000 liter. Urea plant, 3000-5000 liter		10-25 kg NH_3 per ton NH_3 manufactured	High nitrogen content toxic to fish; also promotes eutrophication. Phosphatic fertilizers give Phosphorous in wastes.
3	Metal plating	1-25 liter per liter of plating solution.		1-15 mg CN per liter. 3-100 mg Cr per liter. 0-25 mg Ni per liter.	May have toxicity problem and sludge, CN^-, Cr, Cd, Zn, etc. affect stream life. Some substances persist in food chain.
4	Cane sugar	500 liter/ton	0.6 kg/ton	-	Food industry wastes, in general, contain much organic matter whose degredation leads to depletion of DO in streams and esturies and likely effects on aquatic life such as fish. Odorous and anaerobic conditions may be created.

Table3.5 Water requirement and characteristics of some selected industry wastes.

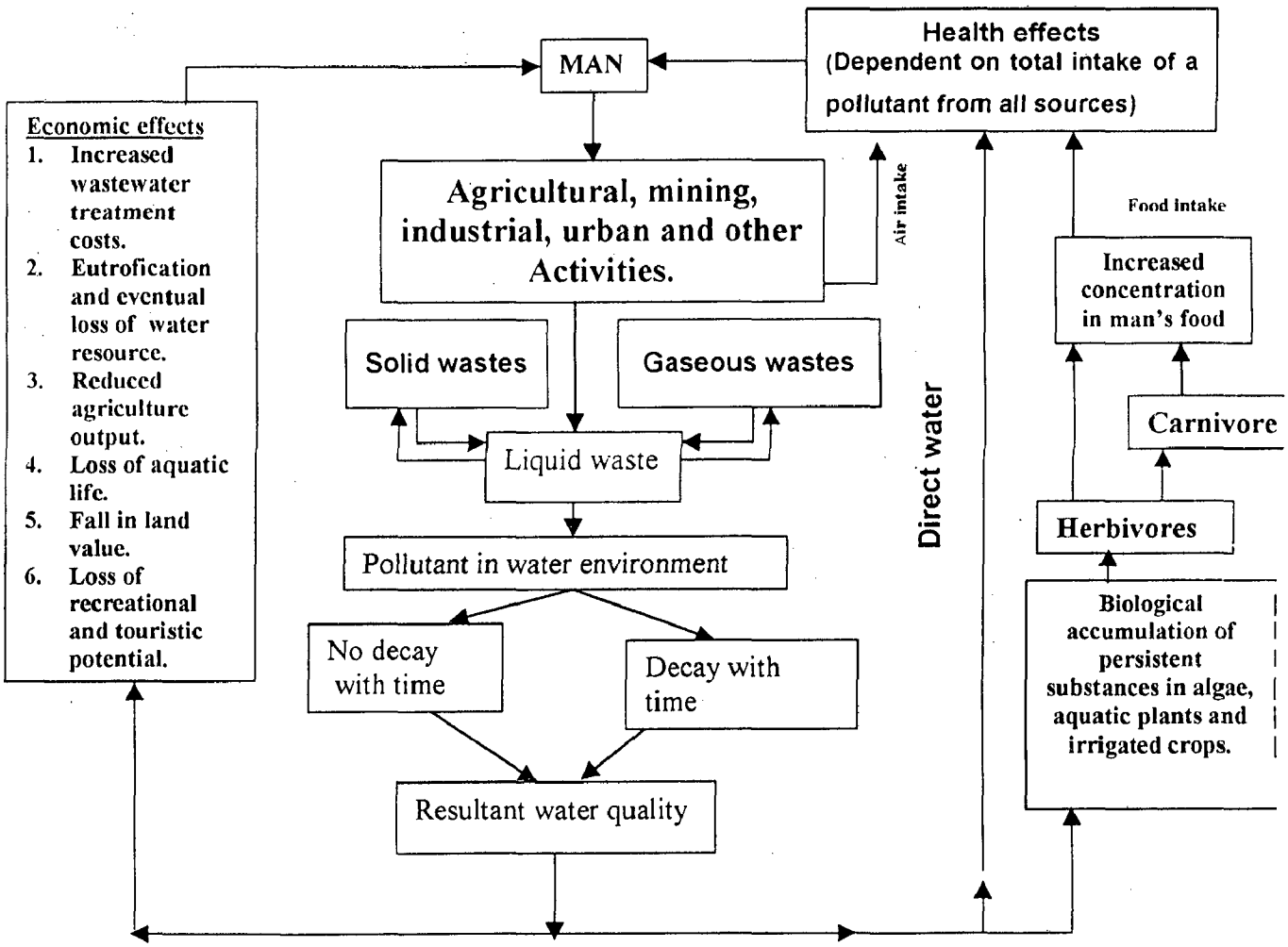


Fig. 3.1: Some health and economic effects likely to results from discharge of solids, liquid and gaseous wastes into water.

Chapter 4

LITERATURE REVIEW

4.1 GENERAL

A comprehensive review is presented here on studies which had been carried out for removal of various pollutant viz. Heavy metals (Cr, Zn, Ni, Cu, Hg etc.), phenolic compounds, dyes and few others organic compounds using low cost adsorbent like bagasse fly ash, carbon slurry, sun flower stalks, rice husk, blast furnace sludge etc. as well as high cost adsorbent like activated carbon.

Table 4.1 lists several papers relevant to the present investigation

Table 4.1: Studies on removal of different pollutants from waste water using low cost adsorbant

References	Adsorbent	Adsorbate / object of study	Operating condition	Conclusion
Allen et al. (1989)	Sphagnum peat	Astrazone yellow 7GL	Batch agitated vessel	Intra-particle diffusion in the peat pore structure is proposed as a mass transfer mechanism
Bailey et al. (1999)	-	-	-	Use of low cost adsorbent have been investigated as a replacement for current costly methods of removing heavy metals from solution
Das and ndyopadhyay (1993)	Low cost natural medium (Vermiculate)	Nickel	Batch studies	• Naturally occurring vermiculate can be used as a low cost adsorbent for nickel removal from solution as both kinetics and isotherm are highly favorable. • Equilibrium partitioning of Ni onto vermiculate can be described by the Freundlich Isotherm. • Adsorption of Ni is found to be appreciable at pH greater than 4.0. • Spent vermiculate can be regenerated by acid treatment and can be reused.
Gajghate and Reddy (1989)	-	-	-	For predicting BOD from COD, quadratic models are recommended for different waste studied and except the dairy industry for which, a cubic model is recommended.

Gangsun et al. (1997)	Sunflower stalks	Basic dyes - Methylene Blue, Basic Red-9 Direct dyes - Congo Red with Direct Blue-71	Batch agitated vessel	• The maximum adsorption of two basic dyes on sunflower stalks are very high, i.e., 205 and 317 mg/g for Methylene Blue and Basic Red-9, respectively • Two direct dyes have relatively lower adsorption on sunflower stalks • Within 30 minutes about 80% of the basic dyes were removed from the solution • The pith, which is the soft and porous material in the centre of stalks, has twice the adsorptive capacity of the skin.
Gangsun et al. (1998)	Sunflower stalks	Heavy metals Cr(III), Cd(II), Cu(II), Zn(II)	Batch agitated vessel	• Reasonably good adsorption capacity for these metals ions. • Adsorption process follow Langmuir Isotherm & coulambic interaction between sunflower stalks & metal ions. • Take up rates of Cr(III), Cd(II) and Cu(II) were very rapid.
Gomez-serrano et al. (1998)	Heat treated and sulfurized activated carbon	Mercury, Cadmium and Lead	Batch Reactor	• The removal of these metal ions can be greatly enhanced by heating the activated carbon either in H_2S from 363 K to 1173 K or first successively in SO_2 and H_2S at room temprature and then in N_2 573 K.
Gupta et al. (1997)		Phenols, viz., 2,4,6 trinitrophenol, 4-chlorophenol, 1,3-dihydroxy benzene	Column	It was observed that 70 ml of 50% w/w NaOH or 50 ml of acetone are sufficient for almost complete desorption of phenols. After regeneration with 1 M HNO_3, the sorption capacity of the column is almost the same as that of virgin adsorbent material.
Gupta et al. (2000)	Activated carbon obtained from carbon slurry	Phenolic compounds	Column studies	• Activated carbon obtained from carbon slurry exhibits very good adsorption properties. • This adsorber can be used in a large scale fixed bed adsorber.
Kapadia et al. (2000)	Flyash	Copper	Batch reactor studies	• Fly ash can effectively adsorb copper present in the liquid effluent at pH around 6.0. • Contact period of 1 hr gives optimal removal. • Adsorption involved is surface phenomenon. • Flyash treatment raises the pH of effluents. • No change in chemical parameters of effluents.

Kim et al. (1990)	Activated carbon	COD	Batch process	Adsorption capacity of of activated carbon increased by 5 times at an equilibrium COD concentration of 100 mg/l after the anaerobic treatment.the capacity is increased by approx. 3o times at the above equilibrium concentration after the anaerobic/aerobic treatment.
Koli et al. (1997)	Flyash	Chromium Cr (VI)	Batch stduies	Activated carbon can be used for removal of higher concentration of chromium but flyash may be better adsorbent to remove lower concentrations of chromium economically.
Kumar et al. (2000)	Activated bagasse carbon, activated jute carbon, thermal power plant ash.	Reduction of COD of wastewater	Batch studies.	• Thermal power plant ash can successfully be used as adsorbent for paper mill effluent. • More than 90% removal efficiency. • All the used adsorbents show good performance at high initial COD level and high temprature.
Kumar et al. (1987)	Flyash	Phenols	Batch process	Satisfactory adsorbent for phenols, however the contact times required to reach equilibrium are larger in comparison with those activated carbon. Fairly steep nature of the Freundlich isotherm for flyash gives a positive indication regarding its use in column adsorbers.
Lopez-delgado et al. (1998)	Blast furnace sludge (BFS)	Heavy metals Pb(II), Cu(II), Cd (II), Cr(III), Zn(II)	Batch studies	• BFS is effective sorbent of these meta ions and performs well over a wide range of concentration. • Langmuir isotherm were better fitted to the process with the exception of the adsorption of Cd and Zn which also showed satisfactory correlation with freundlich isotherms.
Maheshwari *et al* (1999)	Thermal power plant ash	Pulp and paper mill effluents	Batch	Effective adsorbent for pulp and paper mill effluents, shows more than 90% removal efficiency.
Mall et al. (1994)	Bagasse fly ash and activated carbon	Organic matter	Batch	Bagasse fly ash is quite comparable to activated carbon in its adsorptive properties and therefore can be good substitute of activated carbon for the treatment of wastewater from sugar mills.
Mall et al. (1996)	-	-	-	Critical review of non-conventional materials for treatment of industrial waste water, it was concluded that easily available and economical materials can serve as alternates to more costly activated carbon/activated carbon.

Mall et al. (1998)	BFA and activated carbon	2-chloro phenol and 4-chloro phenol	Batch	On the basis of the investigation, it was concluded that bagasse fly ash, which is a waste from sugar mill bagasse fired boiler, can be a potential substitute for activated carbon. The process will be more attractive in integrated sugar mill paper mill complex.
Mall et al. (2001)	Bagasse fly ash, rice husk fly ash and activated carbon	2, 4 dichloro phenol	Batch	The practical applicability of bagasse fly ash and rice husk fly ash in batch operations and various parameters such as effect of contact time, adsorbent dose, pH, etc. has been studied. The removal of 2,4 dichlorophenol shows first order rate expression and equilibrium adsorption data suited well for both Langmuir and Freundlich isotherms. Economic evaluation of BFA and RHFA with the AC shows that their use will be viable.
Mall and Prasad (1998)	Pyrolysed bagasse char (PBC)	Removal of COD	Batch studies	PBC was found effective for removal of COD from pulp & paper mill effluent in the polishing stage.
Mehrotra and Dwivedi (1988)	Raw rice husk, raw bone powder, burnt rice husk, burnt Bone powder and human hair	Chromium (VI)	Batch studies	• Rate of sorbents was found to be highest at pH-2 for all sorbents tried. • Of all the adsorbents tried, hair and burnt rice husk exhibit good sorption capacity. However effectiveness is at low pH only. • The slope obtained from freundlich for hair chromium (VI) system at pH-2 and initial Cr(VI) concentration of 12,500 micro gram per litre gives a very steep slope meaning that oit is very useful for column adsorption operation.
Nag et al. (1999)	Chemically treated saw dust	Chromium-VI and Arsenic(III)	Saw dust beds	95 % removal of chromium and 68 % removal of arsenic achieved.
P. Nageswara Sarma et al. (2000)	Powdered activated carbon	Organic compounds in waste water from p-nitrophenol industry	Batch	Treatment using powdered activated carbon, chemical oxidation by hydrogen peroxide and ozone have been carried out. It has been found that of the three methods, adsorption using activated carbon is the most effective method for the treatment of the effluent under investigation in the laboratory.
ao Venkata B. et al. (2000)	Activated carbon, alumina and bauxite, silica, chitin, natural polymeric adsorbents	Azo-dyes (uses pyridine as precursor)	Batch and Column	Adsorption process can effectively be employed for removal of dyes from water and waste water

Sekar. D et al. (1998)	Powdered activated carbon	Colour removal of distillery spent wash	Batch	The colour removal was found to be 18% only with untreated effluent sample. However, on pre treatment with polyelectrolyte as a flocculating agent, the colour removal drastically increases to 99%.
Sharma and Forster (1993)	Sphagnum Moss Peat	Cr(VI)	Batch and column studies	• Peat exhibit acidic properties in solution and is effective adsorbent for Cr(VI). • Best results are obtained in the pH range 1.5-3.0.At very low pH Cr(VI) reduces to Cr(III), which is poorly adsorbed • The kinetic batch reaction rates are such that a reasonable residence time seems necessaryfor a complete treatment of chromium in peat column. Chromium is adsorbed more rapidly and more efficiently when lower concentrations are used. • An increase in temperature from 25 to 40 °C almost double the maximum adsorption capacity. • The Cr (VI) adsorption on to peat is a chemisorption reaction and the peat –Cr (VI) bond is so strong that 1 M NaOH treatment of metal laden-peat could not release more than 50 % of the total adsorbed metal. The exhausted peat would require disposal through incineration.
Singh and Mishra (1990)	Chemically treated sawdust	Phenolic compounds	Column studies	Impregnated sawdust can be used for the removal of phenols. Adsorbent material can be used repeatedly three times after regeneration. The impregnated sawdust is superior to the non-impregnated sawdust, on account of its affinity for ligands.
Singh and Tiwari (1997)	Carbon slurry	Chromium	Batch studies	Excellent adsorptive properties for removal of Cr (VI)
Srivastava et al. (1987)	Activated carbon developed from carbon slurry generated from fertilizer plants	Heavy metal ions Cr, Hg, Pb, Cu, Mo	Batch and column studies	This adsorbent exhibits good adsorption properties for chromium, mercury & lead and reasonably significant uptake of copper and molybdenum.
Srivastava et al. (1989)	Activated carbon developed from carbon slurry generated from fertilizer plants	Phenols and 2,4-dinitrophenol (DNP)	Batch and column studies	• The adsorbent is effective for removal of phenolic waste. • This activated carbon can easily be recovered.

Vaishya and Prasad (1991)	Sawdust	Copper (II)	Batch Process & column studies	• Sawdust appears to be promising adsorbent for Cu (II) removal from industrial wastewater. • The rate of Cu (II) adosrption on sawdust (mg/g*100) is very high initially and maximum adsorption take place within 1 hr of mixing and decreases markedly from 2 to 6 hr. • Removal of Cu (II) is found 4.4 mg/g for higher copper concentration of 50 mg/l and 0.16 mg/l at adsorbent quantity of 5 g/l in solution. • Isotherm data of Cu (II) sorption can be modeled by both Freundlich and Langmuir isotherms. • Maximum removal occurs at 7.3 pH. • Column study indicate that it is effective in copper removal. It is found that nearly 80% removal takes place in 50 cm adsorbent column.

Chapter - 5
ADSORPTION FUNDAMENTALS

5.1 BASIC CONCEPTS

When two phases, at least one of which is liquid or gas, come into contact, the composition of these phases close to the phase boundary will differ from the composition observed in regions distant from the boundary i.e. within the bulk of the phases. This will occur even though the phases may be in equilibrium. This increase in concentration in the region where the phases are in mutual contact relative to the concentration in the bulk of the phase is called adsorption. Conversely, a concentration decrease may be observed in, for example, solution of electrolytes. This phenomenon is called negative adsorption. The phase in the surface of which a substance from the other phase accumulates is termed the adsorbent and the adsorbed substance is called the adsorbate.

Penetration of particles of one phase deep into the other phase, resembling dissolution to some extent is called absorption. This process may also be accompanied by adsorption, if the particles are irregularly distributed around the phase boundary the majority being concentrated close to the phase boundary. In cases where absorption is combined with adsorption the process involved is most often called sorption.

Adsorption is said to be mono molecular when only one layer of particles (molecules, atoms or dissociated fragments) is involved, when adsorbate concentration may vary over a large distance from the phase boundary the multi-molecular adsorption is involved.

Adsorption may be either physical or chemical. The latter is also known as chemisorption, depending on what process cause the adsorption. In physical adsorption the electron cloud of the substance adsorbed interacts as a whole with the adsorbent and only its polarisation occurs. In chemisorption, on the other hand, electron transfer and sharing of electrons (formation of a new molecular orbital) takes place between the adsorbate and the adsorbent as in the case of normal chemical compounds. Different thermal effects accompany these two types of adsorption. When adsorbed particles are able to migrate along the adsorbent surface, mobile adsorption is involved. When migration does not occur, adsorption is said to be immobile. Sometimes catalyst is also used.

Physical adsorption is independent of the nature of the adsorbent surface, covering surfaces of rather different chemical character with roughly equal numbers of layers at the same pressure. At temperature close to the boiling point of the adsorbate, physical adsorption is reversible. The molecules do not dissociate on physical adsorption. Physical adsorption takes place without any activation energy and its rate should always be proportional to the first order of pressure. A comparison between physical adsorption and chemical adsorption is given in table 5.1.

Table 5.1: Comparison of Physical and Chemical Adsorption

S. No.	Physical Adsorption	Chemical Adsorption
1	Heat of adsorption = 5 kcal/ mole	Heat of adsorption= 20-100 kcal/ mole
2	Adsorption only at temp less than the boiling point of the adsorbate	Adsorption can occur even at higher temperature
3	No Activated Energy involved in the adsorption process	Activation Energy may be involved
4	Mono and multi layer adsorption	Almost mono layer adsorption

5	Quantity adsorbed per unit mass is high i.e. entire surface is participating	Quantity adsorbed per unit mass is low i.e. only active surface sites are important
6	Extent of adsorption depends upon the properties of adsorbent.	Extent of adsorption depends on both adsorbate and adsorbent
7	Rate of adsorption controlled by resistance mass transfer	Rate of adsorbent controlled by resistance reaction.

5.2 ADSORPTION PRACTICES

Adsorption systems are run either on batch or on continuous basis. Following text gives a brief account of both types of systems as in practice.

5.2.1 Batch Adsorption Systems

In a batch adsorption process the adsorbent is mixed with the solution to be treated in a suitable reaction vessel for the stipulated period of time, which depends on the kinetics of adsorption. Agitation is generally provided to ensure proper contact of the two phases. After the equilibrium is attained the adsorbent is separated from the liquid through any of the methods available like filtration, centrifugation or settling. The adsorbent can be regenerated and reused depending upon the case.

5.2.2 Continuous Adsorption Systems

In continuous flow systems the solution to be treated is passed through a bed of adsorbent, which is either fixed, moving or fluidised state. These columns may be used in several stages if necessary. Continuous counter current columns are generally not used for waste water treatment due to operational problems. Fluidised beds have higher operating costs. In certain cases the column may also function as filter bed retaining suspended solids entering with the feed.

5.3 INTRA-PARTICLE DIFFUSION PROCESS

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites. This process can be broken conceptually into a series of consecutive steps

1. Diffusion of adsorbate across a stationary solvent film surrounding each adsorbent.
2. Diffusion through the pores to the immediate vicinity of the internal adsorbent surface
3. Adsorption at an appropriate site

It is assumed that the third step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So it can be assumed that the main resistance to adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the rate limiting step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system propose the term "intra-particle transport" which comprises of surface diffusion and molecular diffusion. Several researchers have shown that surface diffusion is the dominant mechanism and is the rate determining step (Allen et al., 1999; Gupta et al., 1990; Singh et al., 1988). A functional relationship common to most of the treatments of intra-particle transport is that the uptake varies almost proportionally with square root of time.

5.4 ADSORPTION EQUILIBRIA

Adsorbate molecules are simultaneously adsorbed and desorbed from the adsorbent surface. At equilibrium the rate of adsorption equals that of desorption. This equilibrium is of dynamic nature in the sense that the state of

equilibrium changes with the change in the several parameters. Equilibrium behavior is best described by isotherms of adsorption. As the name indicates an isotherm is a plot of amount of solute adsorbed per unit amount of adsorbent against the corresponding equilibrium concentration in the solution phase, temperature remaining constant. Vital conclusions can be drawn from these isotherms, which are useful in the designing of adsorption systems.

A number of isotherm equations have been proposed like Freundlich, Langmuir, Brunnauer-Emmett-Teller(BET), Redlich-Peterson, Toth, and Radke-Prausnitz etc. Out of these the Freundlich and Langmuir isotherm equations have been widely used by many researchers. These two equations have satisfied the data for various organic contaminants and conventional or unconventional adsorbents.

5.4.1 Langmuir Isotherm

The Langmuir isotherm is based on the following assumptions:

Only mono layer adsorption is possible.

1. Adsorbent surface is uniform in terms of energy of adsorption.
2. Adsorbed molecules do not interact with each other.
3. Adsorbed molecules do not migrate on the adsorbent surface.

Langmuir isotherm is obtained from a kinetic derivation of equilibrium between condensation and evaporation of adsorbed molecules. This gives

$$q_e = \frac{q_m . K_A . C_e}{1 + K_A . C_e}$$

where, q_e is the amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium; Ce the concentration of adsorbate solution at equilibrium; K_A the adsorption coefficient (a measure of the adsorption energy) and q_m the amount of adsorbate adsorbed per unit amount of adsorbent required for mono layer adsorption (limiting adsorbing capacity).

The above equation can also be written as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_A \cdot q_m}\left(\frac{1}{C_e}\right)$$

The constants K_A ,q_m can be evaluated from a plot between $1/q_e$ and $1/C_e$ which gives a straight line.

5.4.2 Freundlich Isotherm

The Freundlich isotherm is expressed as:

$$q_e = K_F\ C_e^{1/n}$$

Where, K_F is the adsorption coefficient, which is a measure of adsorption capacity or fundamental effectiveness of the adsorbent. It is directly related to the standard free energy change. Empirical constant 'n' is a measure of the adsorption intensity. The model can be linearised logarithmically as :

$$\log q_e = (1/n) \log C_e + \log K_F$$

Thus a plot between $\log q_e$ and $\log C_e$ is a straight line.

A high K_F and high 'n' value is an indication of high adsorption throughout the concentration range. A low K_F and high 'n' indicates a low adsorption throughout the studied concentration range. A low 'n' value indicates high adsorption at strong solute concentration.

5.4 FACTORS CONTROLLING ADSORPTION

The amount adsorbed by an adsorbent from adsorbate solution is influenced by a number of factors as given below.

5.4.1 Nature of Adsorbent

Both the physical state and chemical nature of adsorbent is important. Adsorbent differs in their specific surface area and affinity for adsorbate. Adsorption capacity is directly proportional to the exposed surface. For the

non-porous adsorbents, the adsorption capacity is inversely proportional to the particle diameter whereas for porous material it is practically independent of particle size. However, for porous substances particle size affects the rate of adsorption. For substances like granular activated carbon the breaking of large particles to form smaller ones open up previously sealed channels making more surface accessible to adsorbent.

Pores may be characterized according to their sizes. Macropores have specific areas in the range of 0.5 to 2 m^2/g. though their contribution to total adsorption is inappreciable, they play a vital role in making the internal parts of the particle available for adsorption. Pores having specific area in the range of 20-40 m^2/g are known as transitional pores and adsorb relatively large molecules or particles of colloidal nature. For micropores the concept of specific area is not important, as the mechanism of adsorption is one of the volume filling rather than the layer to layer filling for macro and transitional pores.

5.4.2 pH of Solution

The surface charge as well as the degree of ionization are affected by the pH of the solution [Elliot et al., 1981). Since the hydrogen and hydroxyl ions adsorbed readily on the adsorbent surface the adsorption of other molecules and ions is effected by pH. It is a common observation that a surface adsorbs anions favourably at low pH and cations in high pH range.

5.4.3 Contact Time

In physical adsorption, most of the adsorbate species are sorbed on the adsorbent surface with in an initial contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium .In physical adsorption most of the adsorbate species are

adsorbed within a short interval of contact time. However, strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of adsorbate species are fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This may be due to the fact that a large number of active surface sites are available for adsorption at initial stages and the rate of adsorption is a function of available vacant site. Concentration of available vacant sites decreases and there is repulsion between solute molecules thereby reducing the adsorption rate.

5.4.4 Initial Concentration

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is very important. The amount adsorbed decreases with increasing adsorbate concentration as the resistance to the uptake of solute from solution of adsorbate decreases with increasing solute concentration. The rate of adsorption is increased because of the increasing driving force.

5.4.5 Temperature

Temperature dependence of adsorption is of complex nature. Adsorption processes are generally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature. This trend may be explained on the basis of rapid increase in the rate of desorption or alternatively explained on the basis of Le-Chatelier's principle.

Some of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to an

increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbent.

5.4.6 Degree of Agitation

Agitation in batch adsorption is important to ensure proper contact between the adsorbent and the solution. At lower agitation speeds the stationary fluid film around the particle is thicker and the process is external mass transfer controlled. With the increase in agitation this film decreases in thickness and the resistance to mass transfer due to this film is reduced and after a certain point the process becomes intra-particle diffusion controlled. Whatever is the extent of agitation, the solution inside the pores remains unaffected and hence, for intra-particle mass transfer controlled process agitation has no effect on the rate of adsorption.

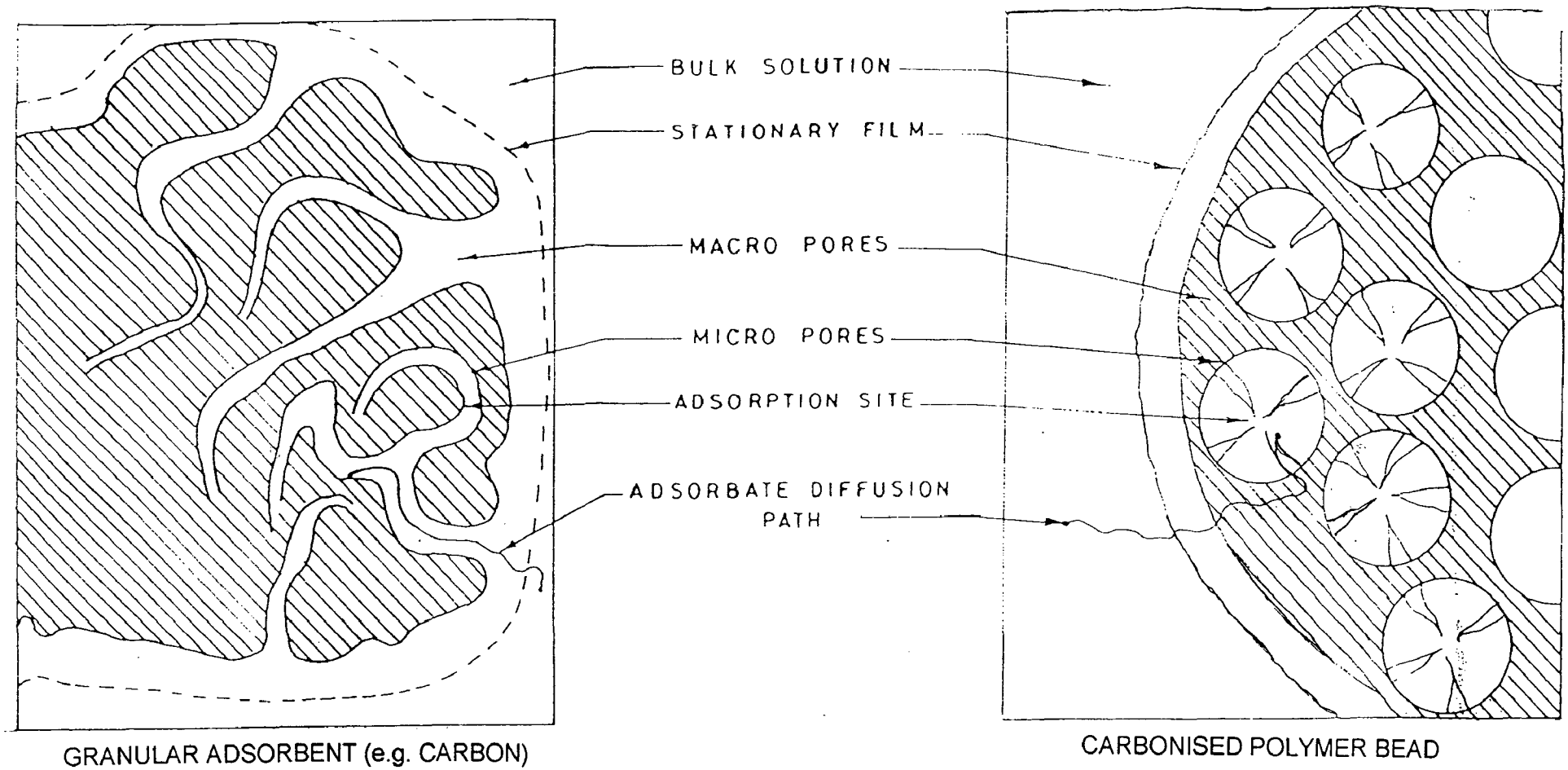


Fig. 5.1 : The Dynamic Adsoprption Process Showing Partial Cross-section of Adsorbent and a Portion of the

Chapter 6

EXPERIMENTAL PROGRAMME

6.1 GENERAL

Batch studies have been carried out for heavy metal (Cr(VI), Ni (II), Zn(II)) bearing synthetic waste water using carbon slurry as an adsorbent. The characterization of the industrial waste water from phenol-formaldehyde plant, polyester industry and for sugar industry were carried out. COD removal experiments were also performed for above stated industrial wastes.

6.2 ANALYSIS OF TYPICAL INDUSTRIAL WASTES

Wastewater samples from phenol-formaldehyde resin plant, polyester industry and from sugar mill were characterized for BOD, COD, DO, suspended solids, dissolved solids, total solids, pH, turbidity, and chlorides. Further COD removal was also studied, after the adsorption on carbon slurry.

6.3 ADSORPTION STUDIES

Dry carbon slurry (CS) has been used as an adsorbent in the present investigation. Carbon slurry has been obtained from National Fertilizer Limited (NFL), Panipat, Haryana, India.

6.3.1 Characterization of Adsorbent

The physico-chemical characteristics of the adsorbent were determined using standard procedures as discussed below.

6.3.2 Proximate Analysis

Proximate analysis of the adsorbents was carried out using the procedure as per IS 1350:1984.

6.3.3 Density

Bulk densities of carbon slurry and was determined by using MAC bulk density meter.

6.3.4 Particle Size

Particle size analysis of the carbon slurry was made using standard sieve analysis as per IS 2720 (Pt 4): 1985.

6.3.5 X-ray Diffraction Analysis

X-ray diffraction analysis of carbon slurry has been carried out by using Phillips (Holland) diffraction unit (Model PW 1140/90), using copper target with nickel as filter media, and K radiation maintained at 1.542 Å. Goniometer and chart speed were maintained at 1° min^{-1} and 1 cm min^{-1}, respectively.

6.3.6 Scanning Electron Microscopy (SEM)

SEM analysis of carbon slurry was carried out by using LEO 435 VP Scanning electron microscope.

6.4 ADSORBATE

Synthetic wastewater solutions of different concentrations (5–50 ppm) were prepared of Chromium (VI), Nickel (II), Zinc (II) by using Potassium Chromate (K_2CrO_4) and chlorides of Nickel and zinc (AR grade). Industrial wastewater samples were obtained from Phenol-formaldehyde resin plant, polyester Industry and sugar Industry.

6.5 Analytical Measurements

The determination of the concentration of Chromium (VI) was done by finding out the absorbance at characteristic wavelength λ_{max} of Cr (VI) using both spectrophotometer (Perkin Elmer Lambda 35) and Atomic Adsorp

Spectroscopy. Standard solutions of Chromium (VI) were taken (5 ppm to 15 ppm) and spectra was scanned. For each concentration max. absorbance was obtained at λ_{max} 540 nm. Calibration curve was plotted between absorbance and solution concentration. The linearity of calibration curves indicates applicability of the Lambert-Beer's Law. This standard calibration curve was used for the determination of residual concentration of Cr(VI). Figure 7.4 represent the calibration curve thus obtained. The Cr(VI) was also determined through atomic adsorption spectroscopy.

Determination of residual concentrations of Nickel (II) and Zinc (II) were carried out only on Atomic Adsorption Spectroscopy. All the experiments for the determination of different concentrations of Nickel (II) and Zinc (II) were carried out by direct aspiration into air acetylene flame. Calibration curve for nickel (II) and zinc(II) is given in Fig. 7.12 and Fig. 7.19, respectively.

6.6 EXPERIMENTAL PROGRAMME

Experiments were carried out for the study of removal of heavy metal bearing wastewater and for the treatment of different industrial effluents as stated below.

6.6.1 Removal of Heavy Metals

To study the effect of important parameters like adsorbent dose, contact time, initial metal concentration batch experiments were conducted for the removal of Cr(VI), Ni(II) and Zn(II). For each experimental run 50 ml of synthetic wastewater of known concentration was taken with known amount of carbon slurry in a 100 ml stoppered conical flask. Synthetic wastewater samples of Cr(VI) were prepared by taking known amount of K_2CrO_4 in distilled water and these samples were agitated in a temperature controlled shaking water bath. The temperature was maintained at 30 ± 1°C. samples were withdrawn at appropriate time intervals. After filtration, the characteristic

colour of Cr(VI) was developed using N-N, di-methyl di-carbazide. The filtrate solution was analysed for remaining concentration of Cr(VI) on spectrophotometer (Perkin elmer lambda 35) at 540 nm wavelength. Solutions for Ni(II) and Zn(II) synthetic wastewater were prepared using chlorides of zinc and nickel (AR grade). These samples were agitated with known amount of carbon slurry, samples were withdrawn at appropriate intervals and analysed for residual concentration by atomic adsorption spectroscopy. For adsorption isotherms, metal solutions of different concentration were agitated with known amount of carbon slurry till equilibrium was achieved. For optimum amount of adsorbent per unit mass adsorbate [Cr(VI)] 50 ml synthetic wastewater was agitated with different adsorbent doses (CS) till equilibrium was attained. Residual concentration of Cr(VI) was then determined.

6.6.2 Treatment of Industrial Effluents

For the study of the effect of adsorption by carbon slurry on COD of phenol formaldehyde resin plant waste, samples of different initial COD were agitated with known amount of carbon slurry till the equilibrium was attained and residual COD of the filtrate was determined. Equilibrium isotherms were plotted. Percentage COD reduction was studied for different samples of polyester industry waste and sugar industry waste using 1 g of carbon slurry as adsorbent for 6 hrs.

Table 6.1 : Operating range for Cr(VI), Ni(II) and Zn(II) for estimating concentration from calibration curve

Sr. No	Sample	Equation of calibration curve	Operating range
1	Chromium (VI)	Y=0.1848x	0 < x < 50
2	Nickel (II)	Y=0.0301 x + 0.0582	0 < x < 50
3	Zinc (II)	Y= 0.1868x	0 < x < 50

Here x = concentration in ppm; Y= absorbance.

Chapter 7

RESULTS AND DISCUSSION

7.1 GENERAL

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include

1. Characterization of carbon slurry.
2. Characterization of wastewater from phenol-formaldehyde resin plant, polyester plant and sugar mill.
3. Batch adsorption studies
   - For adsorption of individual metals from synthetic wastewater.
   - For competitive adsorption of metals in multi-cationic aqueous solution.
   - For removal of COD from industrial waste.

7.2 CHARACTERIZATION OF ADSORBENTS

Carbon slurry (NFL, Panipat, Haryana) has been used as an adsorben in the present investigation. Characteristics of adsorbent (CS) used include bulk density, particle size, proximate analysis and chemical analysis. For the structural and morphological characteristics, X-ray diffraction and scanning electron microscope analysis were also carried out.

Physico-chemical characteristics of carbon slurry are given in Tat 7.1 & 7.2 and the particle size distribution is given in Table 7.3.

The scanning electron micrograph of carbon slurry shows very fine particle size in order of micron and a less porous structure, however due to smaller particle size adsorptive surface area is high.

X-ray diffraction pattern of carbon slurry shows presence of silica compounds like SiO_2 and $CaSiO_3$. The other peak may be due to the presence of Al_2O_3 & Fe_2O_3. d-value characteristics of these compounds are given in Table - 7.4 .

7.3 CHARACTERIZATION OF INDUSTRIAL WASTE

Experiments on wastewater samples from three different industries phenol formaldehyde resin plant, polyester plant and sugar mill have been carried out in current study. These waste have been characterized for their pH, turbidity, total solids, suspended solids, dissolved oxygen, BOD, COD and chlorides. Table 7.5 shows the characteristics of the three wastes. The COD of the waste from phenol-formaldehyde resin plant may be due to high concentration of phenols and other chemicals in the wastewater sample. For the determination of phenols in the wastewater a calibration curve was plotted which is shown in Fig. 7.26.

7.4 BATCH ADSORPTION STUDIES

Batch adsorption studies for removal of heavy metals from synthetic solutions of individual metal ions and from multi-cationic solutions of known concentration have been carried out. The removal of COD from different industrial wastes has also been studied.

7.4.1 Batch Adsorption Studies for Metals

Detailed adsorption studies have been conducted for the removal of chromium (VI), Nickel (II) and Zinc (II) from synthetic wastewater samples

having known concentrations of these metal ions. Effect of various operating parameters, viz. concentration, adsorbent dose and contact time has been studied. Competitive adsorption of these metal ions has been also studied and presented along with these results.

7.4.1.1 Effect of Adsorbent Dose

The effect of adsorbent dose (CS) on removal of chromium (VI) is shown in Fig. 7.5 and the results are tabulated in Table A-2. It can be seen from the figure that the percentage removal increases up to a certain limit and then it remains almost constant beyond the dose of 1.0 g of carbon slurry. For larger concentration of adsorbent the adsorption sites are more and the adsorbate molecules have to travel considerable distance in order to reach these sites. So no effect does it make on further increase in adsorbent dose.

7.4.1.2 Effect of Contact Time

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment.

Figure7.6, 7.13, & 7.20 for Cr(VI), Ni(II) and ZN(II) respectively show the effect of contact time on their removal from the synthetic wastewater solution of known initial concentration. The results are shown in Table A-3, A-10 and A-17 respectively. It is found that rate of removal is very rapid during initial 30-45 minutes and thereafter it starts decreasing and there is no significant change after 300 minutes. This can be explained on the basis of the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after some time, the remaining vaca

surface sites are difficult to occupy due to repulsive forces between the solute molecules of the solid and bulk phases.

7.4.1.3 Effect of Initial Concentration

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is very important. The amount adsorbed decreases with increase in adsorbate concentration as the resistance to the uptake of solute from solution of adsorbate decreases with increase in solute concentration. The rate of adsorption is increased because of the increasing driving force.

The effect of initial concentration for removal of chromium (VI), Nickel (II) and Zinc (II) is shown in Fig.7.7, Fig. 7.14and Fig. 7.21 and the calculated values are given in Table A-4, A-10,A-18 respectively. From the figures, it is evident that percentage removal decreases with the increase in initial concentration of adsorbate solution.

7.4.1.4 Kinetics of Adsorption

Kinetic modelling of removal of heavy metals by carbon slurry has been carried out by using lagergren model. (Mall et al., 1996; Kumar et al., 1995).

$$\frac{q_e - q}{q_e} = \exp(-kt)\,(q_e - q) / q_e = \exp(-kt)$$

where q_e = Amount of adsorbate adsorbed at equilibrium, mg/g

q = Amount of adsorbate adsorbed at time t, mg/g.

k = Adsorption rate constant, min^{-1}

t = Time, min.

This equation can also be expressed as

$$\log(q_e - q) = \log q_e - \frac{k}{2.3} t \quad \log (q_e\text{-}q) = \log q_e - kt / 2.303$$

The plot of log (q_e – q) against time is shown in Fig. 7.8, 7.15, 7.22 for chromium (VI), Ni (II) and for Zinc (II) respectively and the results are tabulated in A-5, A-12 and A-19. The straight-line plot shows the validity of Lagergren equation.

The correlation coefficients (R) obtained after fitting experimental data to Lagergren equation are given in Appendix-A23. This follows that adsorption kinetics can fairly be assumed to be of first order. Table 7.6 gives the value of adsorption rate constant (K) for different adsorbates with carbon slurry.

7.4.1.5 Intra-particle Diffusion Study

A functional relationship commonly used to describe the intra-particle transport is the plot between mass of solute adsorbed per unit mass of adsorbent (q) and square root of contact time ($t^{0.5}$). The linear nature of the plot shows that the controlling mechanism for adsorption is intra-particle diffusion (Allen et al, 1989). These plots for chromium (VI), Nickel (II) and Zinc (II) are shown in Figs. 7.11, 7.18 and 7.25, respectively and the results are tabulated in A-8, A-15 and A-22. The plot of q_e versus $t^{0.5}$ is found to be linear for a wide range of contact time for all the three metal ions chromium (VI), Nickel (II) and Zinc (II). The correlation coefficients (r) for fitting the experimental data to straight line are given in A-23. Thus indicating that controlling step is intra-particle diffusion. The values of intra-particle diffusion rate parameters (in mg g^{-1} $min^{-0.5}$) are given in Table 7.8.

7.4.1.6 Adsorption Isotherm Equations

Various isotherm equations have been used to describe the equilibrium nature of adsorption. Some of these equations are Freundlich, Langmuir, Redlich-Peterson, Radko-Praunitz and Toth equations. Out of these Freundlich and Langmuir isotherm equations are widely used by researchers in the field of environmental engineering. The Freundlich isotherm is represented by the following equation ;

$$q_e = K_F C_e^{1/n}$$

which can also be written as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

The Langmuir isotherm is represented by the following equation

$$q_e = \frac{q_m K_A C_e}{1 + K_A C_e}$$

Which can also be written as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_A q_m}\left(\frac{1}{C_e}\right)$$

Fig. 7.9, 7.16 & 7.23 give the plot of log q_e for Cr(VI), Ni(II) and Zn(II) and corresponding results are shown in A-6,A-13, A-20. Fig. 7.10, 7.17 are the plots of of $1/q_e$ Vs $1/C_e$ for Cr(VI), Ni(II) and Zn(II) and corresponding results are shown. Langmuir isotherm was found applicable in all cases studied. The experimental data fairly fit the straight line as shown by correlation coefficients (r) given in table A-23..

The values of parameters for Freundlich and Langmuir isotherms are given in Table 7.7. The value of separation factor or equilibrium constant R_L which is defined as $R_L = 1/(1 + bC_i)$ (where C_i is initial concentration and b is

Langmuir constant) indicates the nature of adsorption as (Foust, S. D. and Alay, O. M., 1986)

R_L	> 1	Unfavourable
R_L	= 1	Linear
$0 < R_L$	< 1	Favourable
R_L	= 0	Irreversible

The values of R_L for Cr(VI), Ni(II) and Zn(II) are also given in 7.7 the value of R_L is found to be less than 1 for all the three metals so adsorption using carbon slurry is favorable. The values of 1/n were also found to be less than 1. So, it again proves adsorption to be favourable.

7.4.1.6 Competitive Adsorption for Multi-Cationic Solution

50 ml synthetic wastewater sample10 ppm of each of chromium (VI), Nickel (II) and Zinc (II) was taken in 100 stoppered conical flask and 1 gm of carbon slurry is added to this. It was agitated in a temperature controlled shaking water bath at a constant temperature 30 ± 1°C for 6 hrs. Removal of chromium (VI), Nickel (II) and Zinc (II) in competitive environment are reported in Table 7.9.

7.4.2 Batch Study for the Removal of COD from Industrial Wastewater

The most important criterion in the quality of wastewater is COD. This parameter receives more attention while designing any waste treatment plant. Waste samples of different initial COD from three different sources are treated and the effect of adsorption on COD is studied.

7.4.2.1 Phenol Formaldehyde Plant Waste

A typical industrial wastewater from above mentioned industry was taken and diluted to form solutions of varying initial COD. Removal of COD was studied using carbon slurry as adsorbent. Percent removal thus observed was plotted against initial concentration (Fig. 7.27). Equilibrium data was plotted to see the applicability of Freundlich and Langmuir isotherms given in Fig. 7.28 and Fig. 7.29, respectively. The values of adsorption parameters are given in Table 7.12. The straight line obtained shows the applicability of both the isotherms. The value of 1/n as well as R_L was found to be less than 1. So, we can say the adsorption prove to be favourable.

7.4.2.2. Polyester and Sugar Industry Waste

Treated and untreated combined waste from polyester plant was treated with carbon slurry and removal of COD was measured. About 67% and 81% COD removal was observed for untreated and treated wastewater respectively. It also shows that percentage removal is high in case of low concentration effluent.

Combined waste water from a sugar mill was also treated with carbon slurry and about 86.4% COD removal was adsorbed. Complete removal of colour could also be seen.

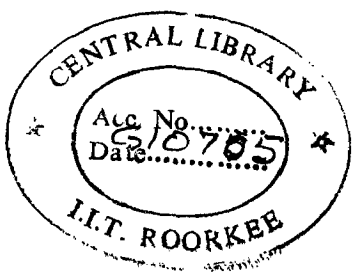


Table 7.1 : PROXIMATE ANALYSIS OF ADSORBENT

S. No.	Adsorbent	Surface Moisture (%)	Inherent Moisture (%)	Ash %	Volatile Matter (%)	Fixed Carbon (%)	Bulk Density (kg/m^3)
1	Carbon Slurry (NFL, Panipat)	10.74	4.85	5.2	13.33	76.62	308.03

Table 7.2 : CHEMICAL ANALYSIS OF CARBON SLURRY

Adsorbent	Loss on ignition (%)	Insoluble residue (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)
Carbon Slurry (NFL, Panipat)	-	90.3	79.13	9.56	4.22	2.67	2.5

Table 7.3 : PARTICLE SIZE ANALYSIS OF CARBON SLURRY (NFL, PANIPAT)

Sieve Size (μ)	% Weight
>600	9.76
600-500	34.41
500-425	5.66
425-355	14.72
355-250	20.21
250-212	2.70
212-180	1.40
180-150	8.45
<150	2.69

Average particle size : 419.22 micron

Table 7.4 : XRD analysis

Formula Used : $2d\sin\theta = n\lambda$

$\lambda = 1.54Å$, $n = 1$

Sample : Carbon Slurry (NFL, Panipat)

2θ	d
25.0°	3.56
42.0°	2.15

Table 7.5 : Characterization of different Industrial waste

Sr. No.	Characteristic	Polyester Waste		Phenolic Waste	Sugar Industry Waste
		Untreated	Treated		
1	pH	7.1	7.5	5.45	5.08
2	Total solids (mg/l)	800	520	-	1430
3	Suspended solids (mg/l)	45	30	-	1130
4	Dissolved solids (mg/l)	765	490	-	100
5	Turbidity (NTU)	-	-	29.2	166
6	DO (mg/l)	1.6	4.8	0.25	2.1
7	COD (mg/l)	440	147	184000	308
8	BOD_5 (mg/l)	220	40	12985	255
9	Chlorides (mg/l)	-	-	2.5	-
10	Phenols (ppm)	-	-	5000	-

Table 7.6 : Adsorption rate constant K for adsorbent (carbon slurry) in aqueous solutions of Cr (VI), Ni (II) and Zn (II) from Lagergren equation.

Sr. No.	Adsorbate	Lagergren contant $K(min^{-1})$
1	Chromium (VI)	0.2056
2	Nickel (II)	0.8214
3	Zinc(II)	0.1127

Table 7.7 : Isotherm parameter for different adsorbate-adsorbent system and separation factor R_L

Adsorbent	Adsorbate	Freundlich Isotherm		Langmuir Isotherm		R_L
		K_F $(mg/l)^{-1/n}$	n	q_m (mg/g)	$K_A(mg^{-1})$	
Carbon slurry	Cr (VI)	0.7825	1.7191	3.2573	0.2056	0.0101
	Ni (II)	0.4045	4.0420	0.8288	0.8214	0.0386
	Zn (II)	0.3756	1.9829	2.3392	0.1127	0.0140

Table 7.8 : Intra-particle diffusion rate parameter k from Weber-Morris plot

Sr. No.	Adsorbate	k $(mg\ g^{-1}\ min^{-0.5})$
1	Chromium (VI)	0.0208
2	Nickel (II)	0.0739
3	Zinc(II)	0.0108

Table 7.9 : Results obtained on treating multicationic aqueous solution with carbon slurry as adsorbent

Metals	Initial Concentration (ppm)	Final Concentration (ppm)	% Removal
Cr(VI)	10	1.2	88
Ni(II)	10	5.8	42
Zn(II)	10	4.0	60

Table 7.10 : COD removal for polyester plant waste using carbon slurry

Sample	COD (mg/l) before treatment	COD (mg/l) after treatment	% Reduction
Polyester plant untreated waste	224	74	67
Polyester plant treated waste	132	24	81

Table 7.11 : COD removal for sugar industry waste using carbon slurry

Sample	COD (mg/l) before treatment	COD (mg/l) after treatment	% Reduction
Sugar industry sample	300	42	86.4

Table 7.12 : Isotherm parameter for different adsorbate-adsorbent system and separation factor R_L

Adsorbent	Adsorbate	Freundlich Isotherm		Langmuir Isotherm		R_L
		K_F $(mg/l)^{-1/n}$	n	q_m (mg/g)	$K_A(mg^{-1})$	
Carbon slurry	Phenol formaldehyde resin plant waste (COD removal)	-0.717	10.752	0.332	319.68	2.142×10^{-3}

Table 7.13 : Effect of adsorption by carbon slurry on phenolic wastes of different initial COD

Sr. No.	Initial COD (1×10^3 mg/l)	% decrease in COD
1	135	4.50
2	108	5.60
3	81	7.29
4	54	10.90
5	27	21.70
6	10	49.16
7	5	52.70
8	1	65.00

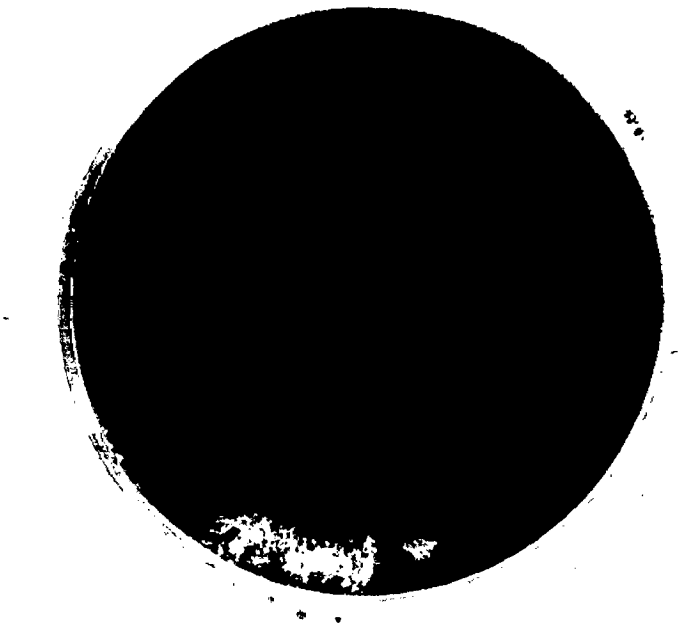


Fig. 7.1 : Photographs of Carbon slurry (NFL, Panipat)

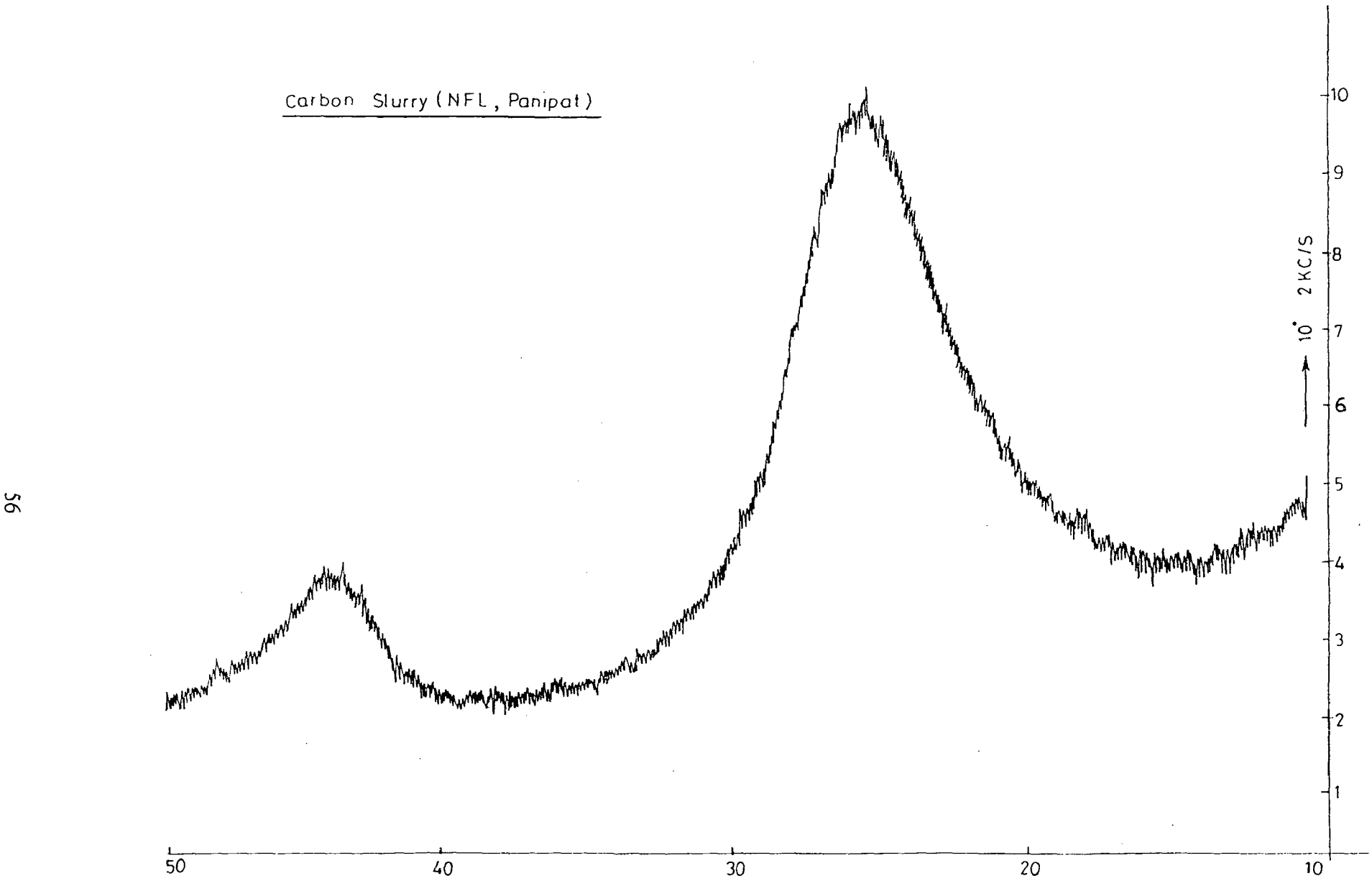
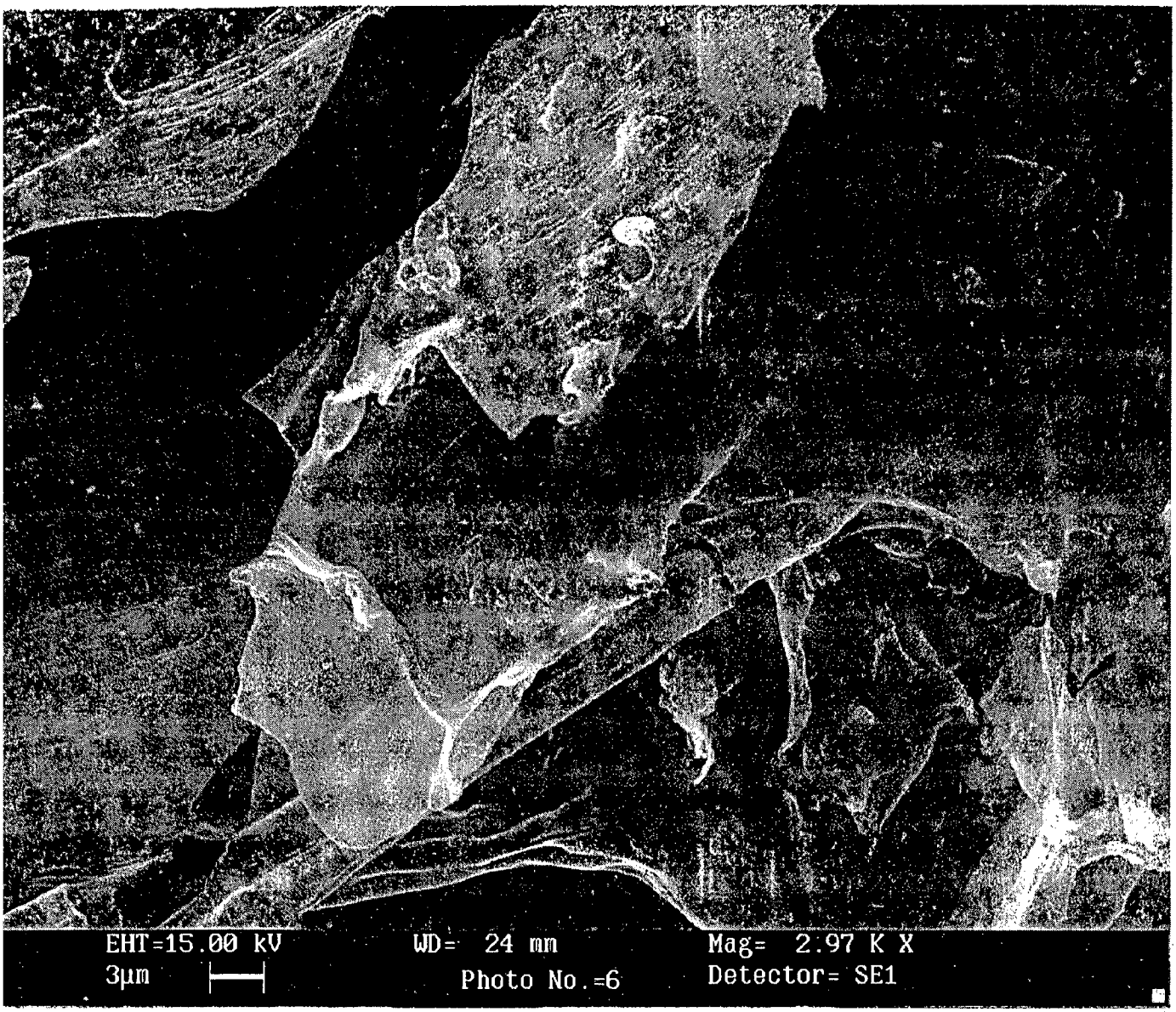


Fig. 7.2 : X-ray diffraction graph



7.3 : Scanning Electron Micrograph of carbon slurry

(NFL, Panipat)

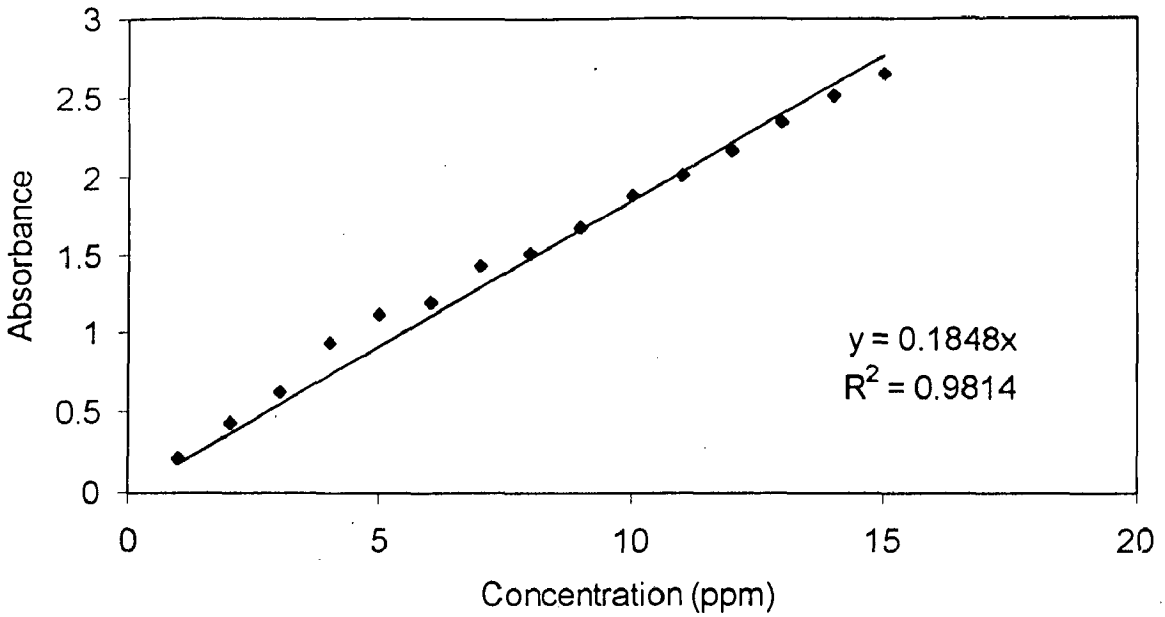


Fig. 7.4: Calibration curve for chromium (VI)

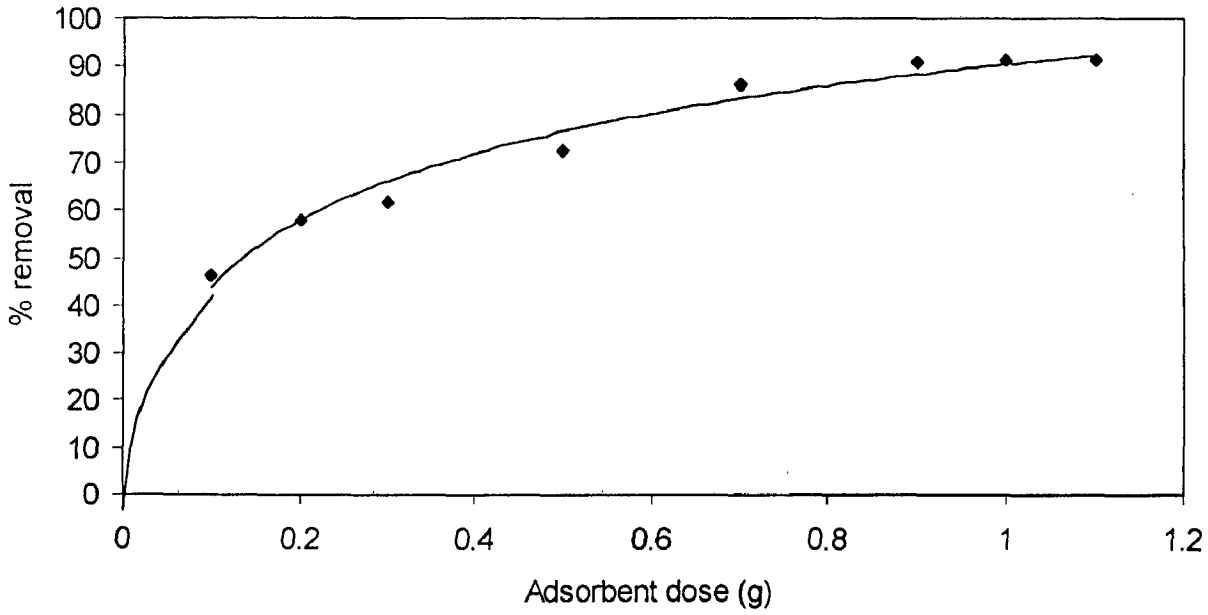


Fig. 7.5: Effect of adsorbent dose on removal of Cr(VI)

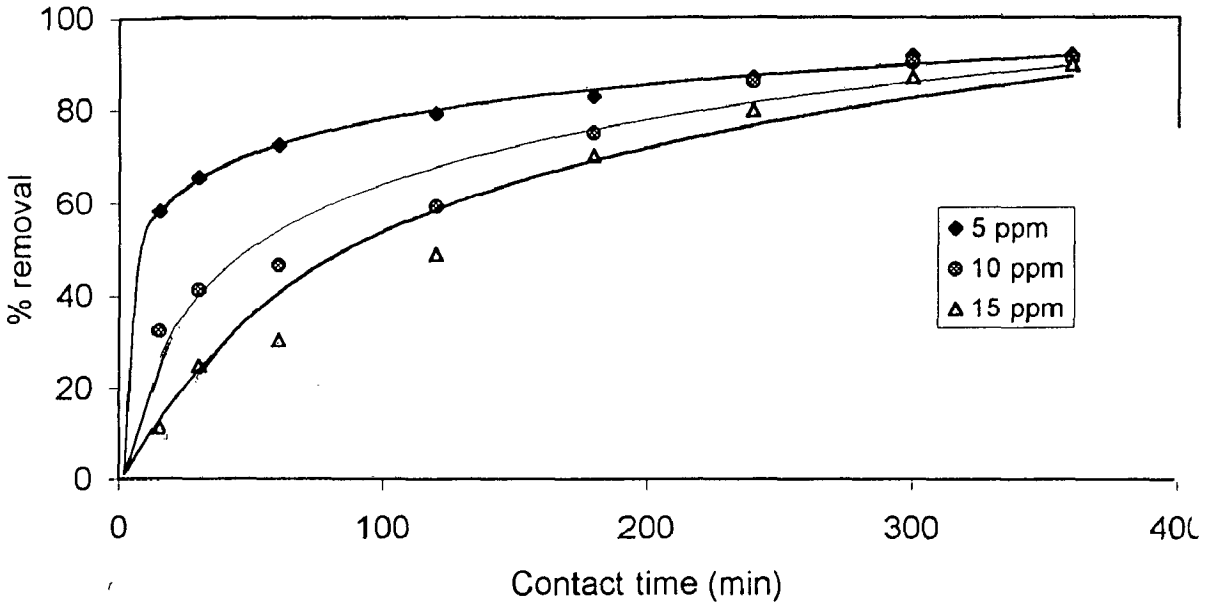


Fig. 7.6: Effect of contact time on removal of Cr(VI)

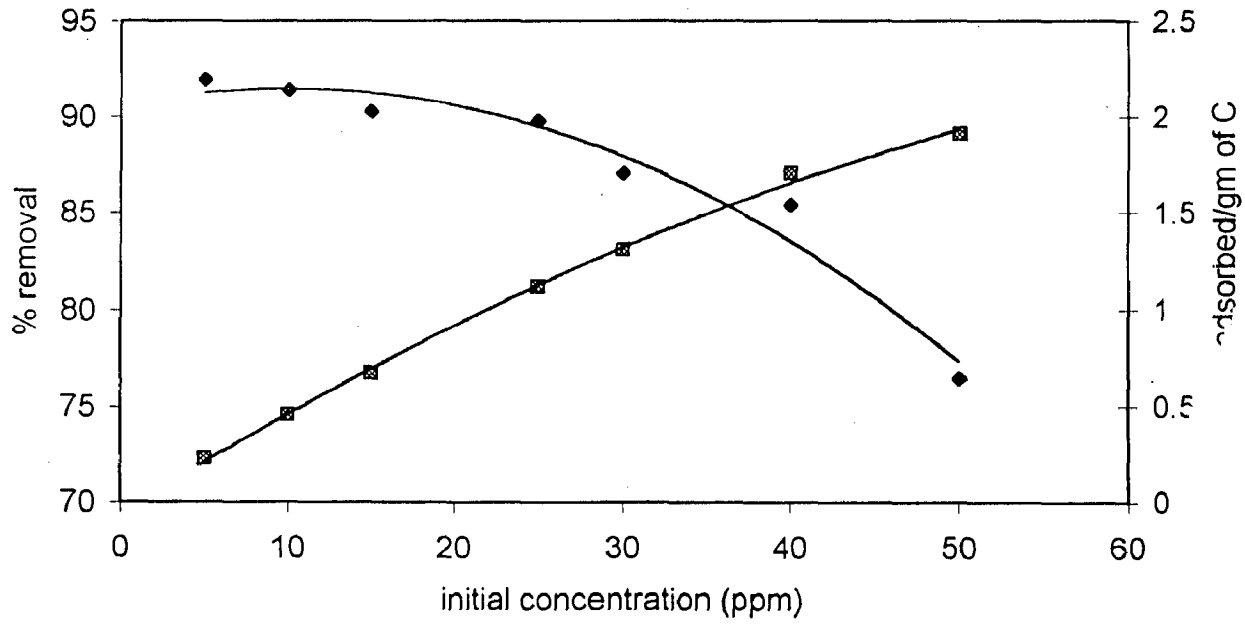


Fig. 7.7: Effect of Initial Concentration on Removal of Cr (VI)

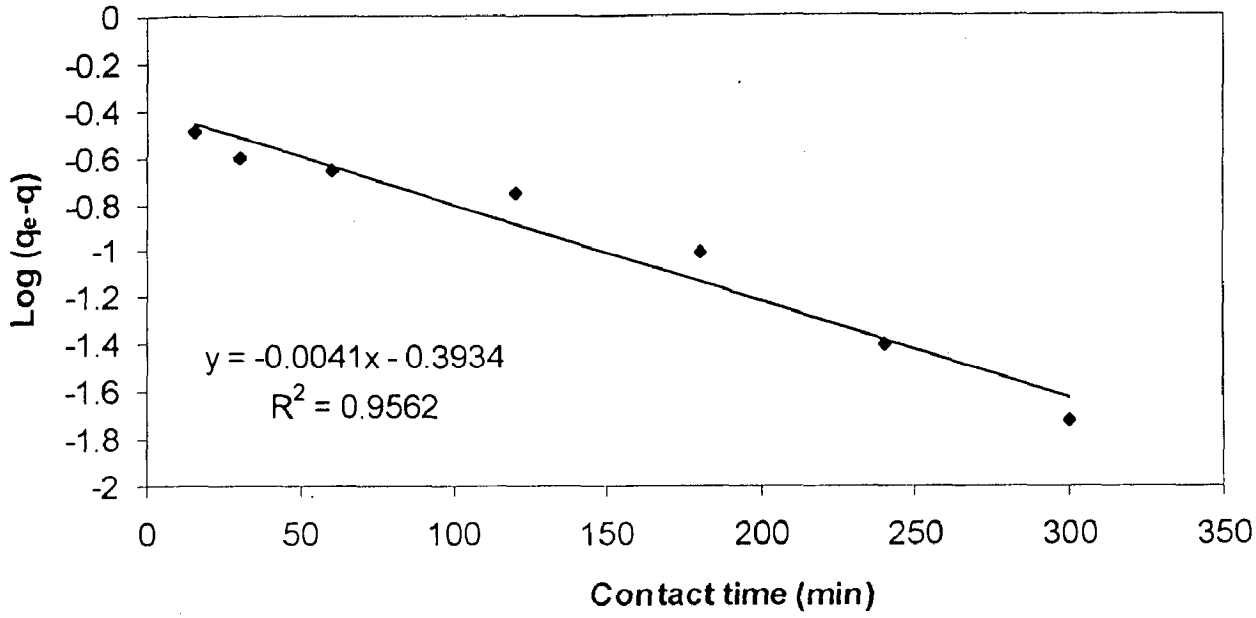


Fig. 7.8 : Lagergren plot for removal of Cr(VI)

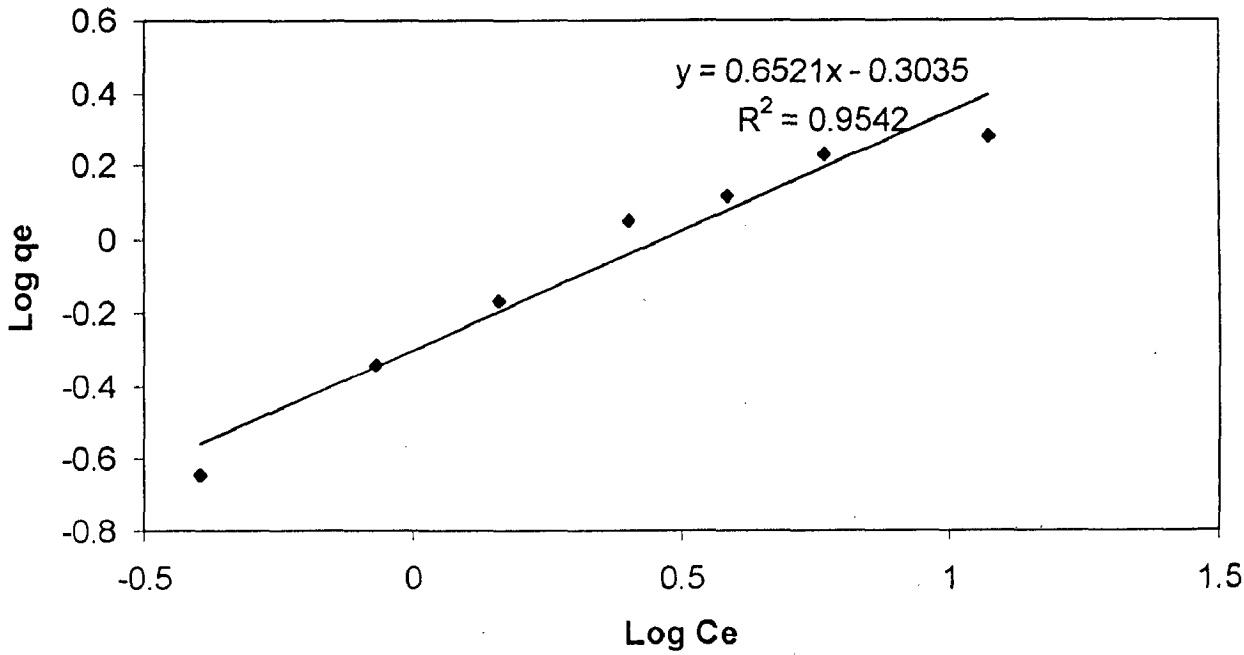


Fig. 7.9: Freundlich Isotherm fore removal of Cr(VI)

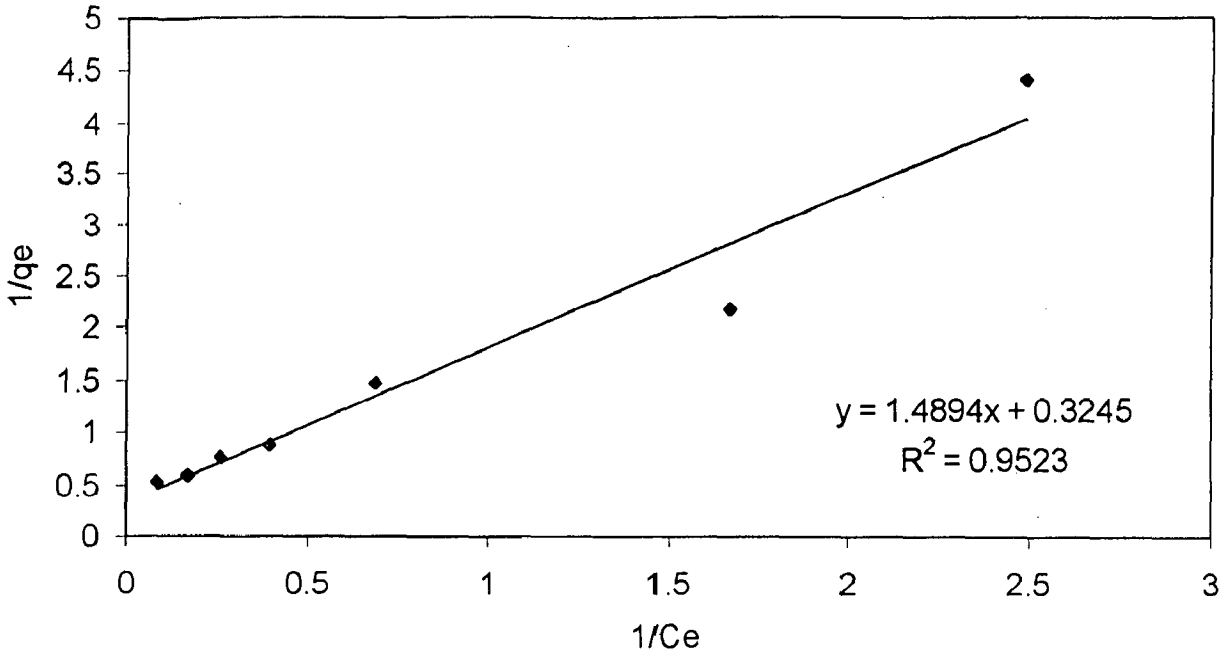


Fig. 7.10: Langmuir Isotherm for removal of Cr(VI)

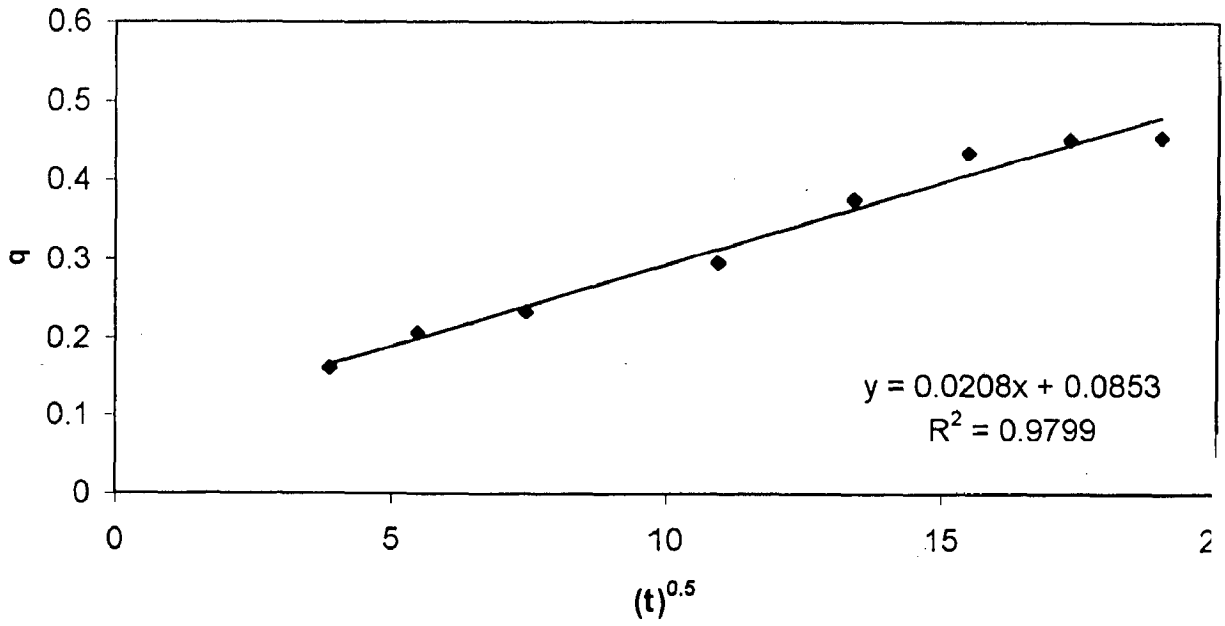


Fig. 7.11: Weber-Morris plot for removal of Cr(VI)

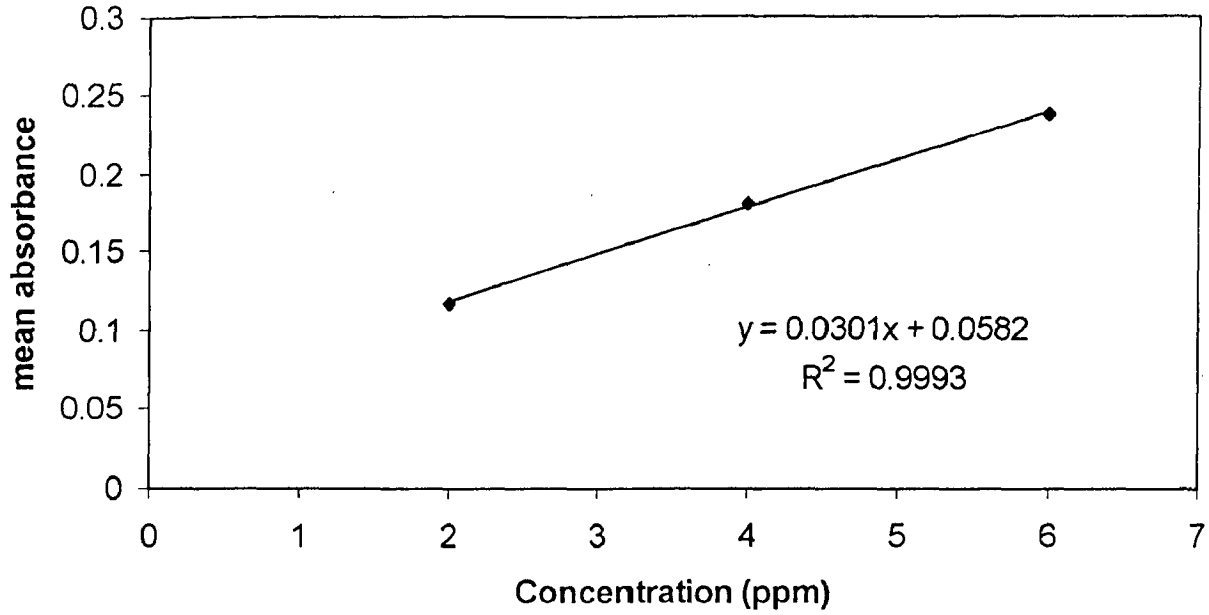


Fig. 7.12: Calibration Curve of Ni (II)

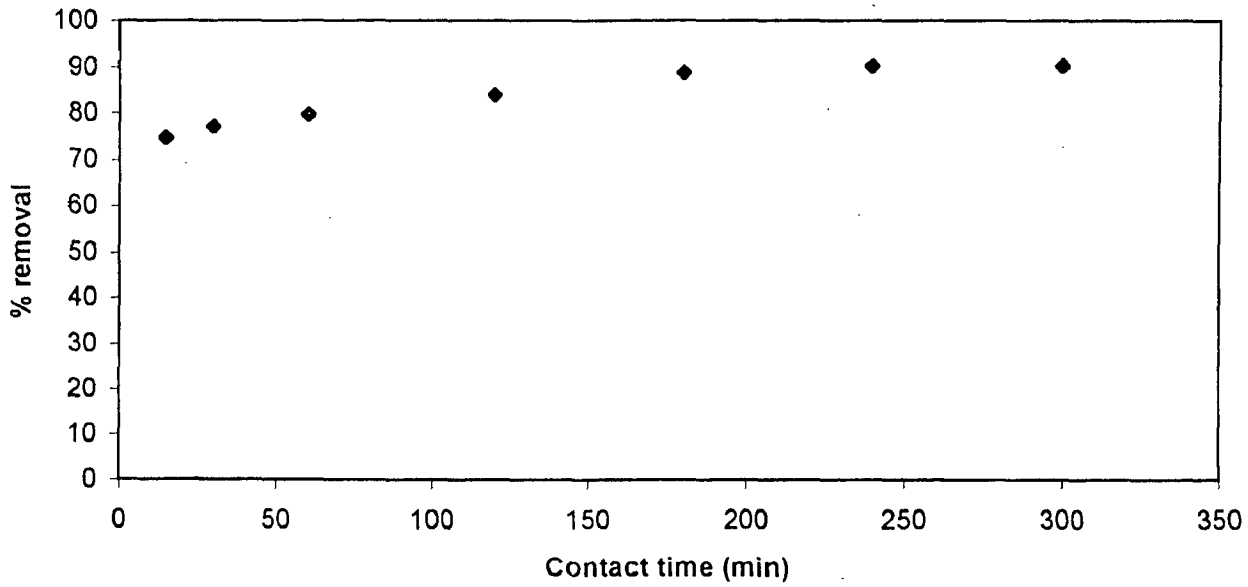


Fig. 7.13 : Effect of contact time on the removal of Ni(II)

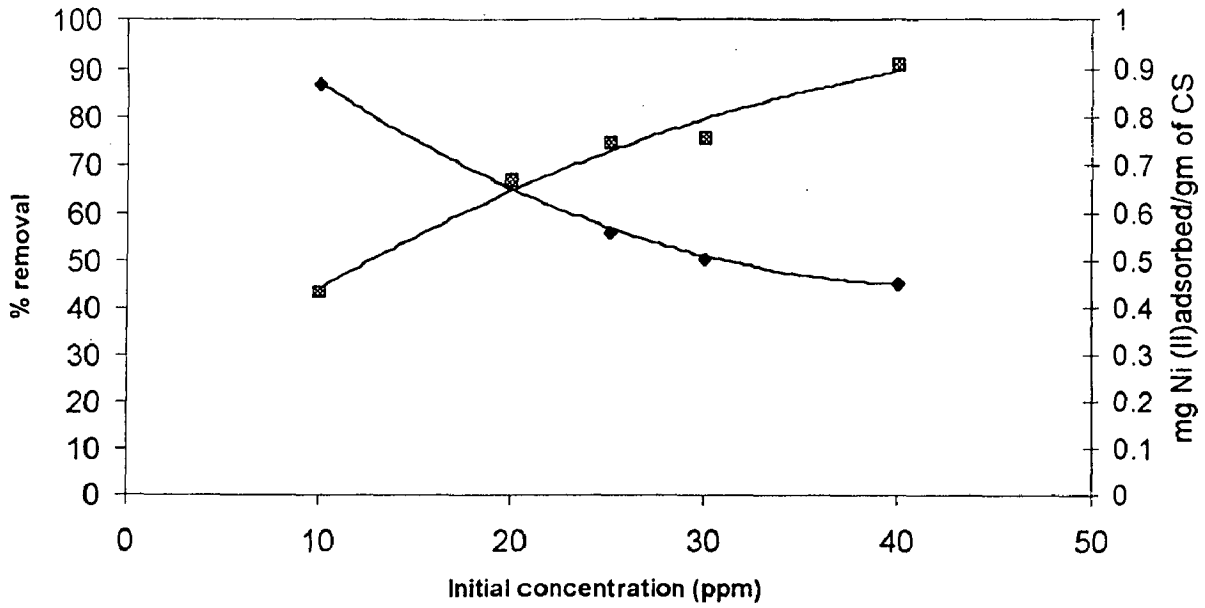


Fig. 7.14 : Effect of initial concentration on removal of Ni(II)

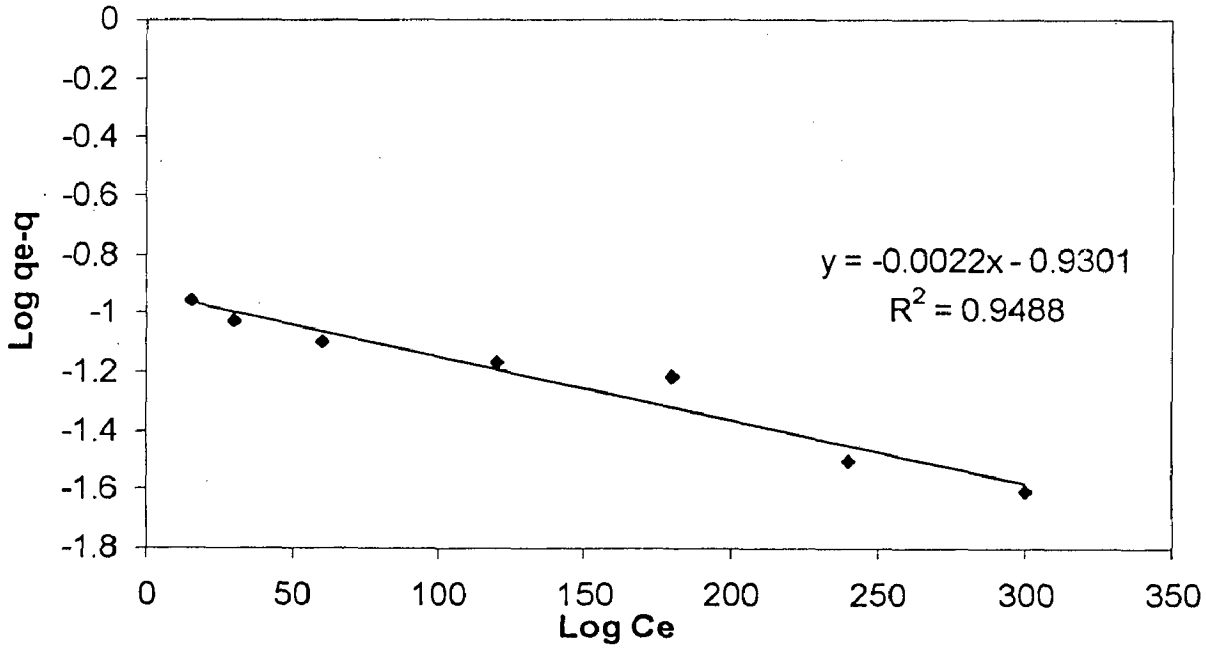


Fig. 7.15 : Lagergren plot for removal of Ni(II)

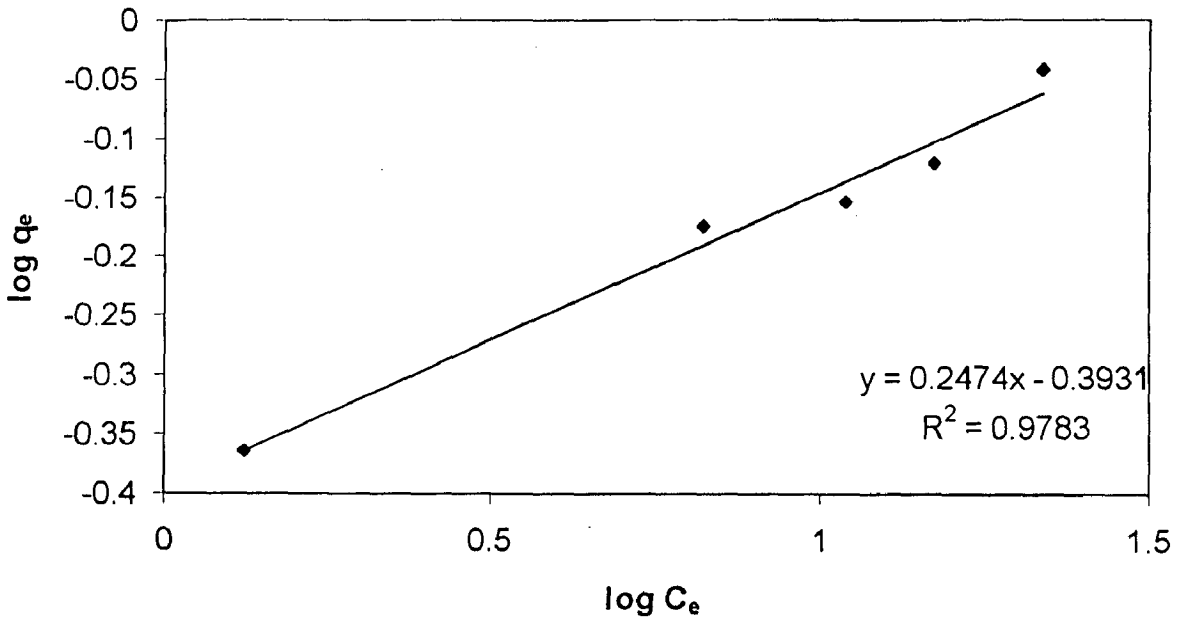


Fig. 7.16 : Freundlich Isotherm for removal of Ni(II)

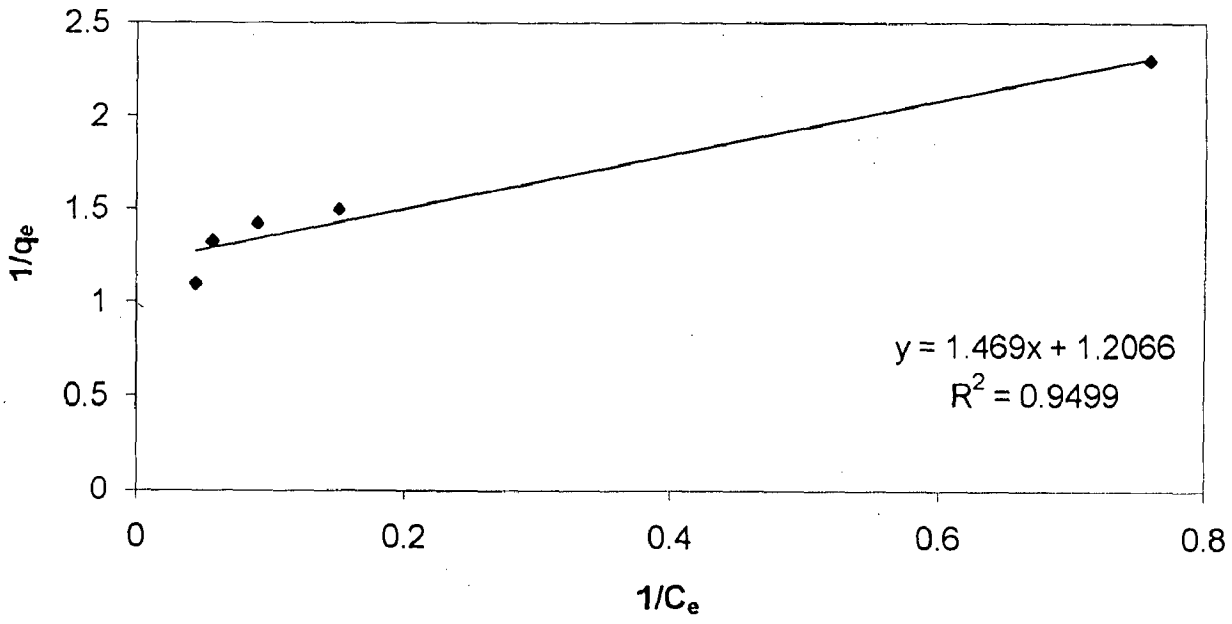


Fig. 7.17 : Langmuir Isotherm for removal of Ni(II)

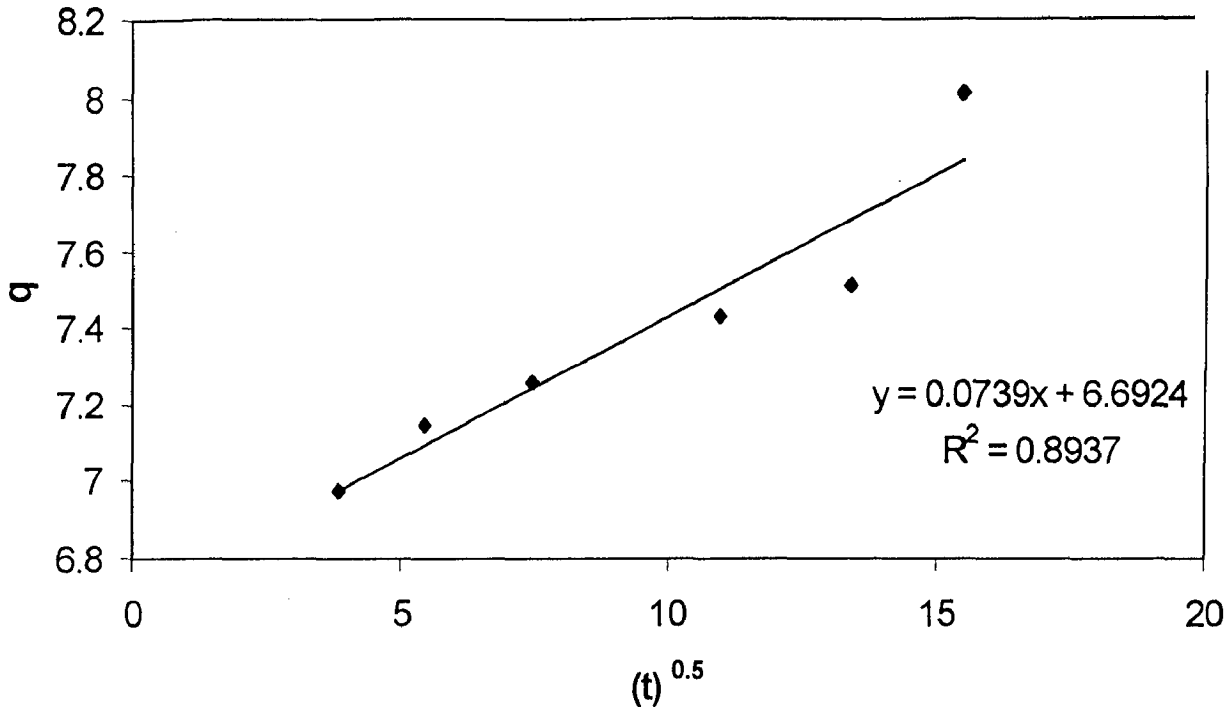


Fig. 7.18: Weber-Morris plot for the removal of Ni(II)

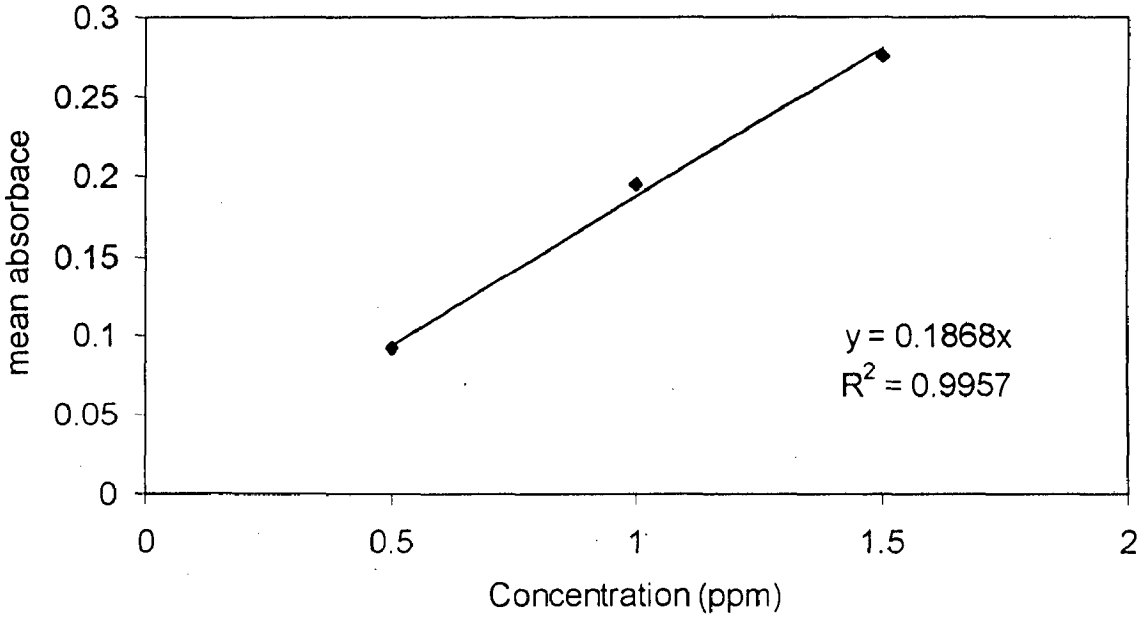


Fig. 7.19 : Calibration curve for the removal of Zn(II)

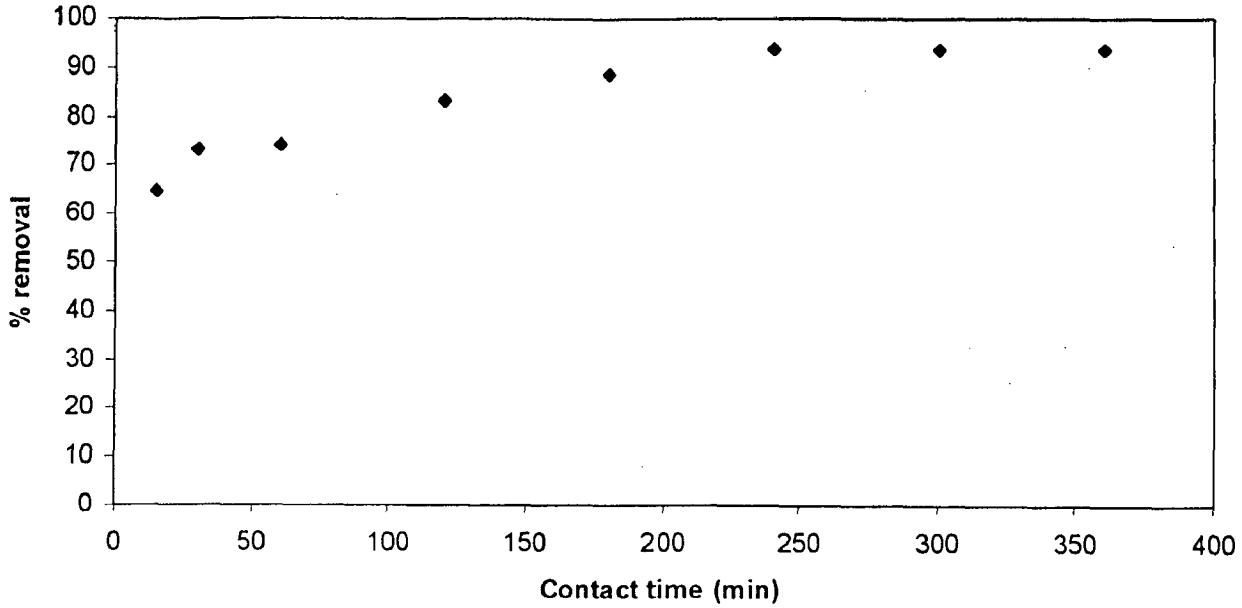


Fig. 7.20: Effect of contact time on removal of Zn(II)

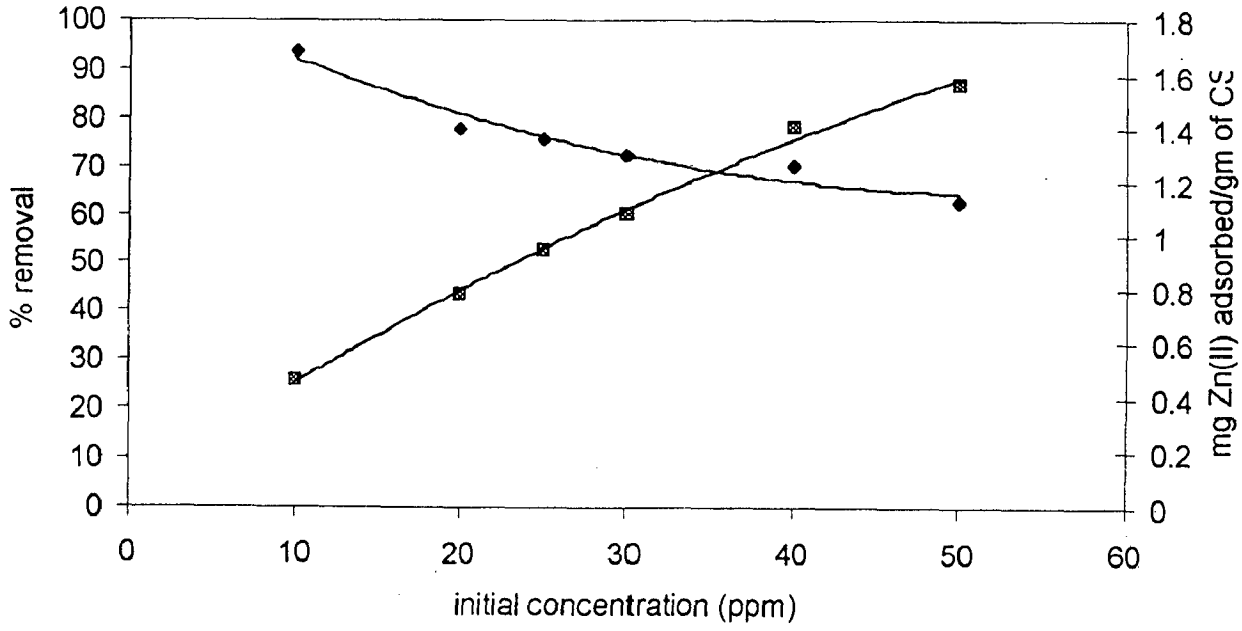


Fig. 7.21: Effect of initial concentration on the removal of Zn(II)

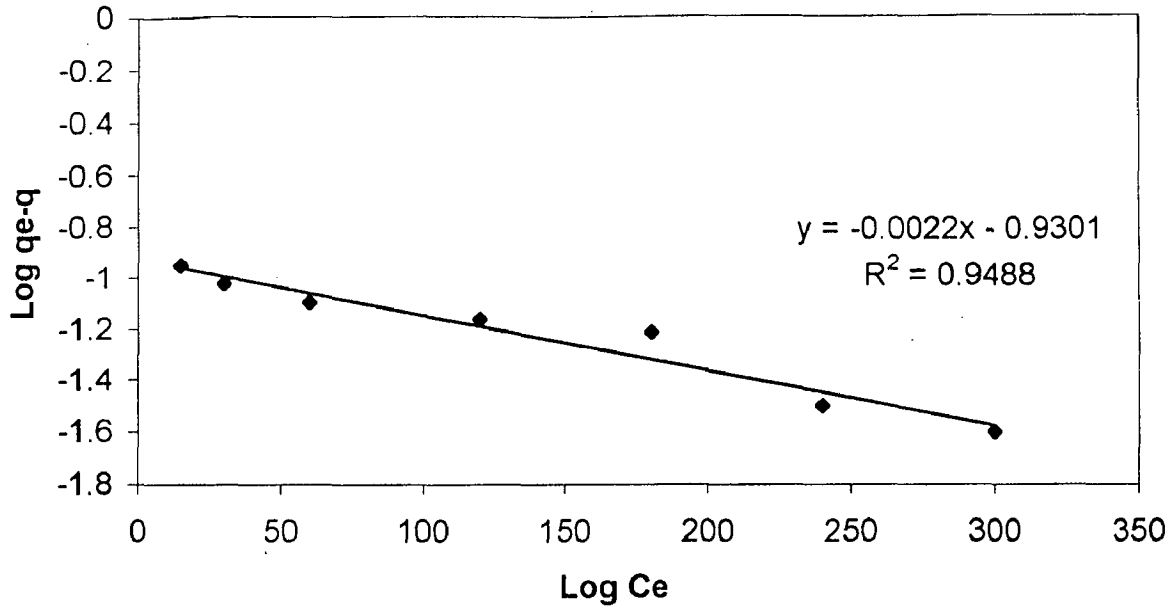


Fig. 7.22 : Lagergren plot for the removal of Zn(II)

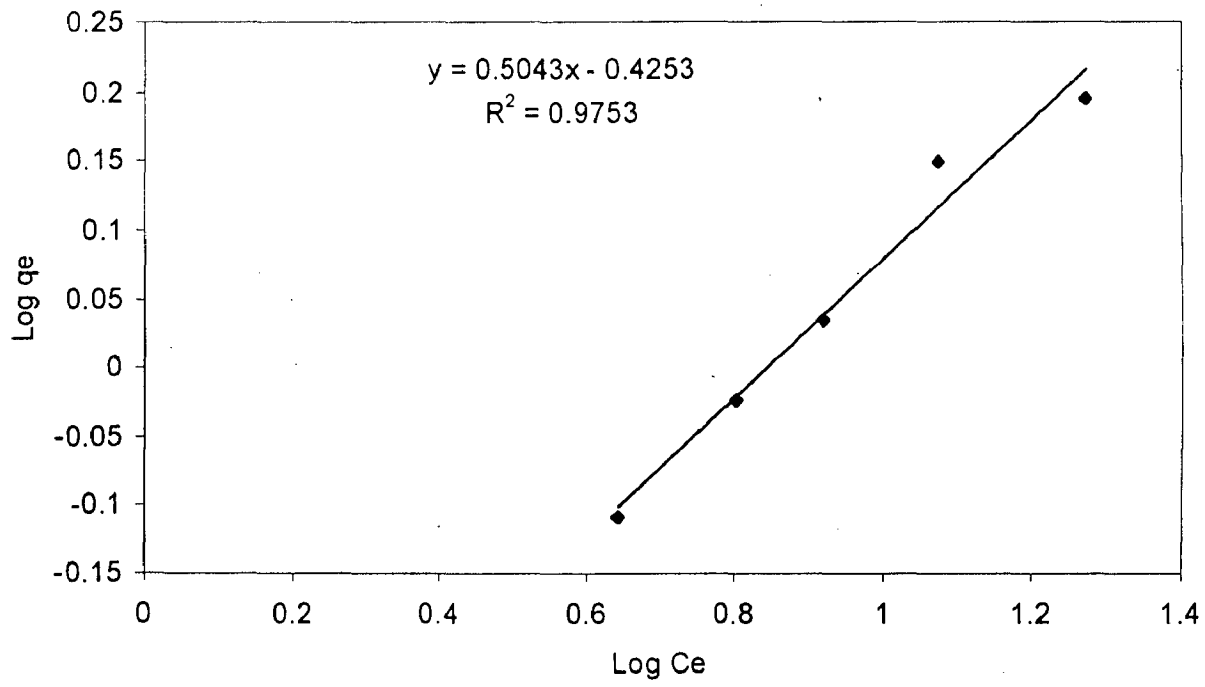


Fig. 7.23 : Freundlich isotherm for the removal of Zn(II)

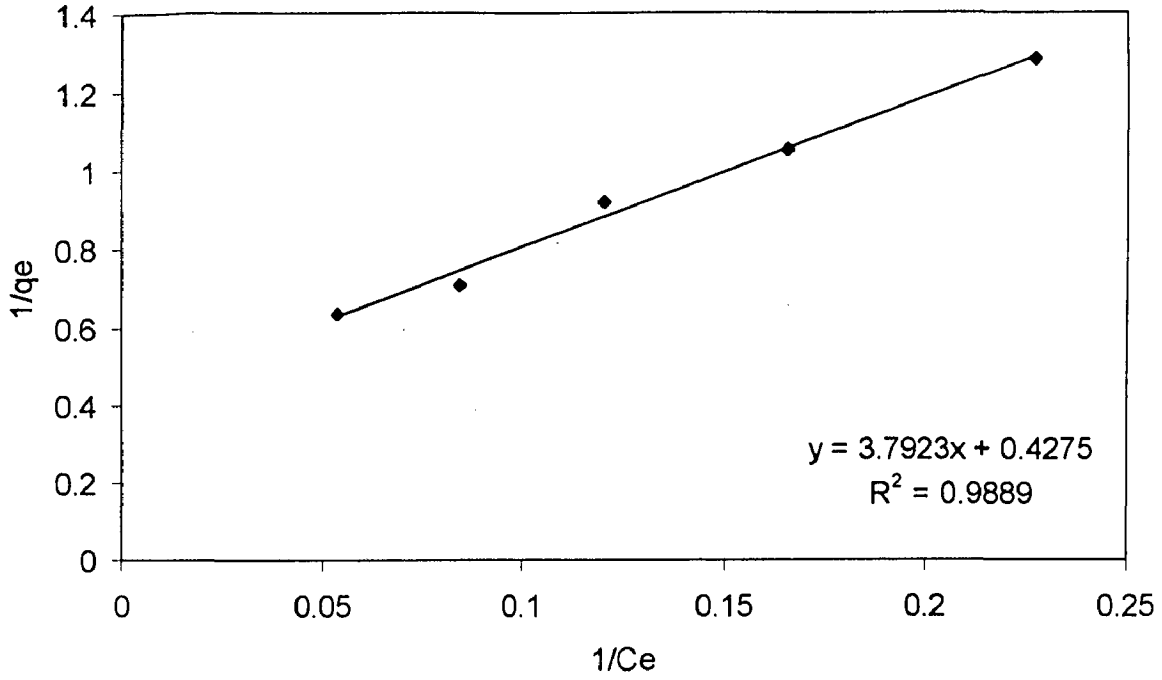


Fig. 7.24: Langmuir isotherm for the removal of Zn(II)

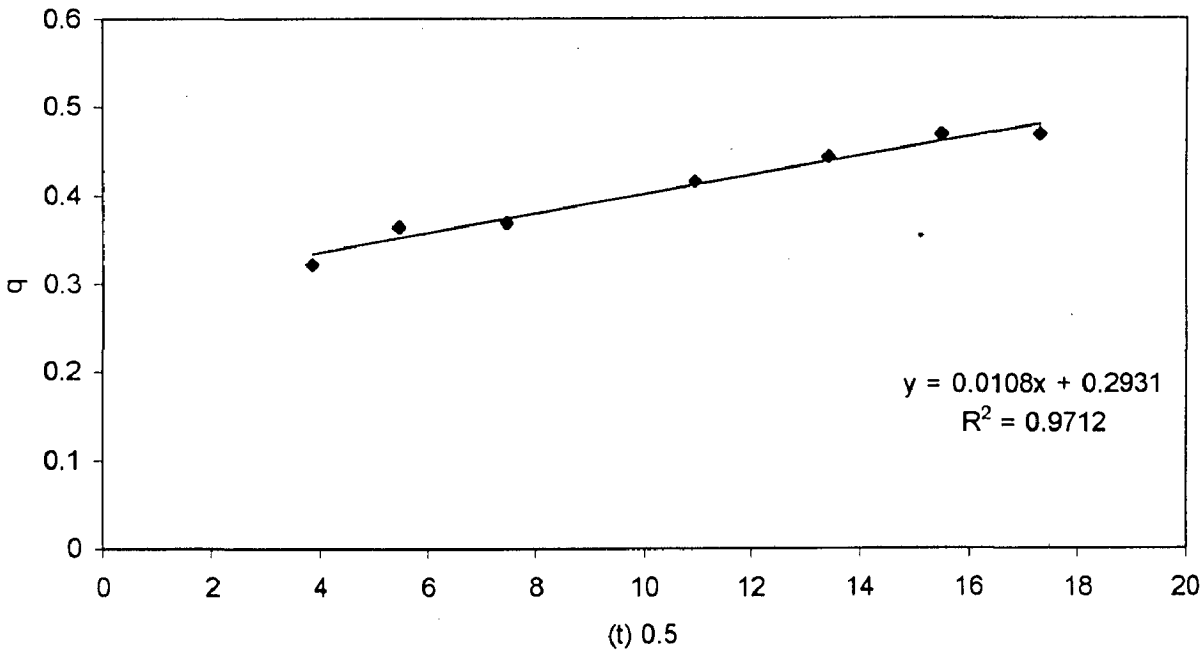


Fig. 7.25 : Weber-Morris plot for removal of Zn(II)

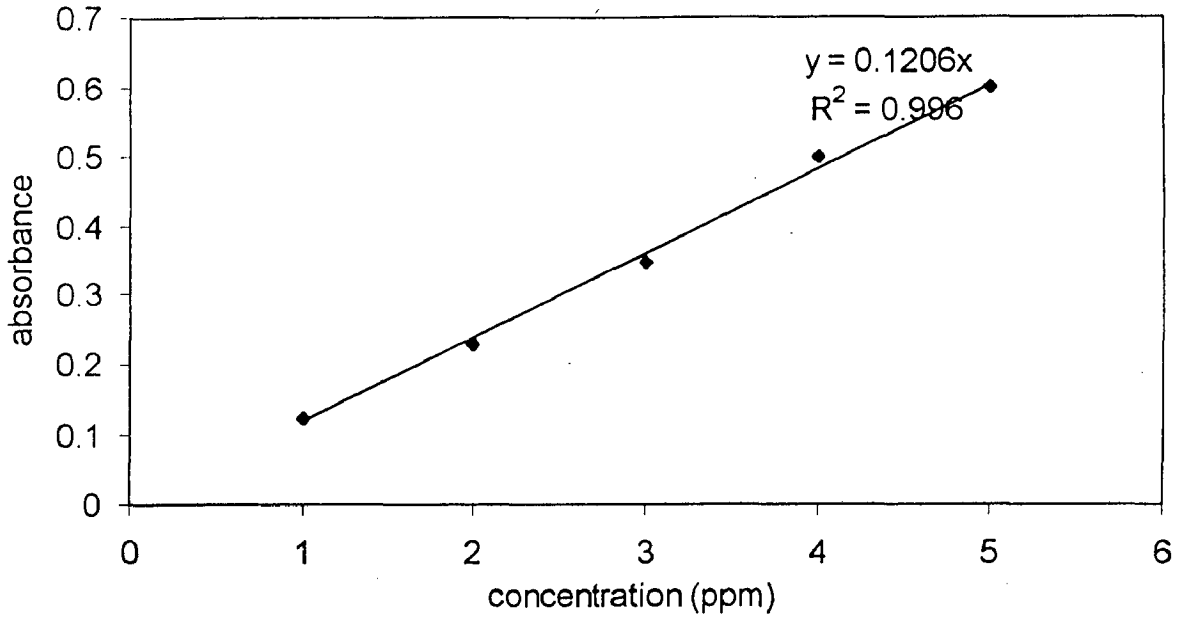


Fig. 7.26 : Calibration curve for phenol

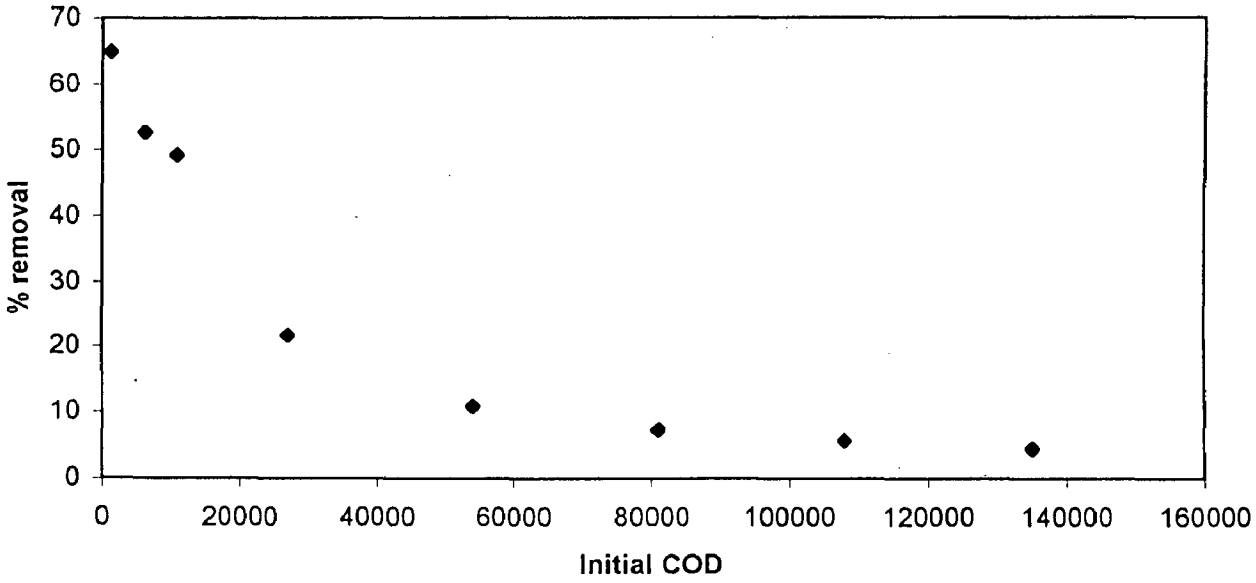


Fig. 7.27 : Effect of initial concentration (COD) on removal of COD from phenol formaldehyde resin plant waste

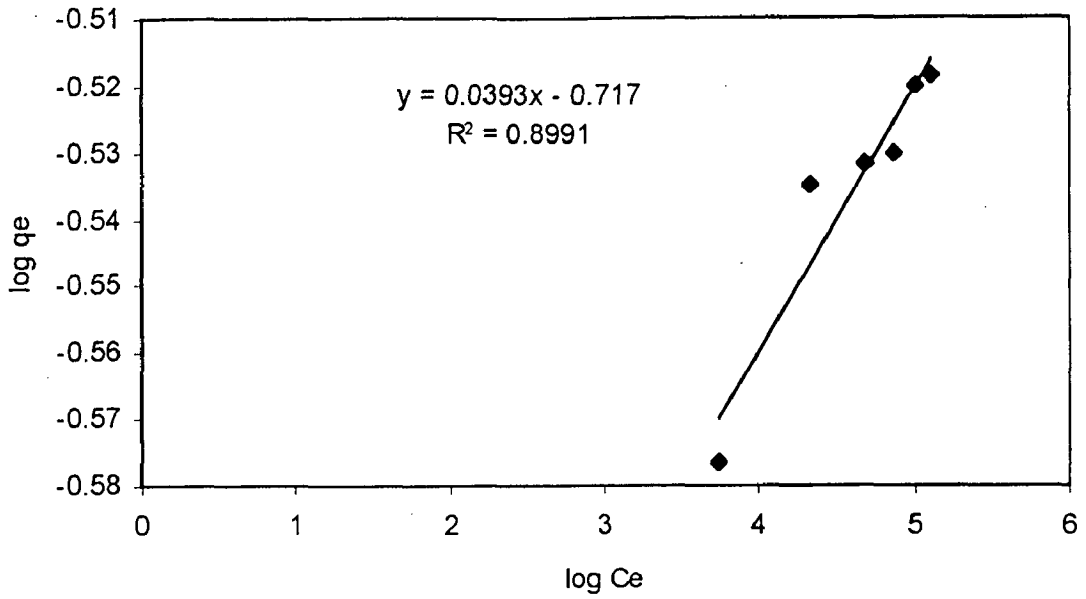


Fig. 7.28 : Freundlich isotherm for removal of COD

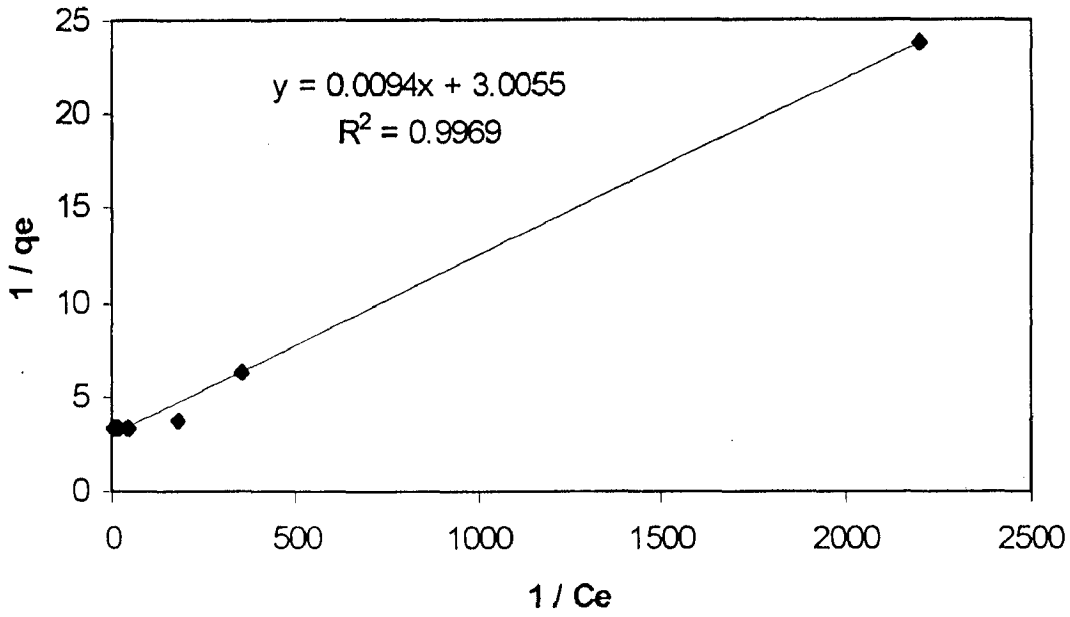


Fig. 7.29 : Langmuir isotherm for removal of COD

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The following major conclusions drawn from the present work are given below :

- Surface area of carbon slurry was found to be 358.3 m^2/g which shows that carbon slurry can be good adsorbent as surface area of commercial activated carbon is also in this range.
- SEM studies reveal that carbon slurry shows very fine particle size in the order of micron.
- X-ray Diffraction studies of carbon slurry indicate presence of $CaSiO_3$, Al_2O_3, MgO, CaO.
- Percentage removal of Cr(VI) was found to increases with the adsorbent dose upto certain optimum dose after which no appreciable removal was found.
- Removal of Cr(VI), Ni(II) and Zn(II) was found to be rapid in initial stages of adsorption followed by slow adsorption upto saturation.
- Percentage removal of Cr(VI), Ni(II) and Zn(II) decreases with increase in their initial concentration.
- In competitive adsorption, Cr(VI) is readily adsorbed in comparison to Ni(II) and Zn(II).
- Carbon slurry is found to be very good adsorbent for the removal of Cr(VI), Ni(II) and Zn(II).
- Percentage of COD removal increases as COD of waste decreases. COD removal to the extent of 86.4%, 81% and 65%

was found in polyester, sugar mill and phenol formaldehyde waste respectively.

- 100% colour removal has been observed in the case of sugar mill effluent.
- Kinetics of removal follows first order rate expression
- Equilibrium data confirms applicability of Freundlich and Langmuir isotherm equations.
- Weber and Morris plot reveals that the pore diffusion is the rate controlling step.
- Carbon slurry has shown excellent adsorptive characteristics for the removal of heavy metals and COD for different wastewater samples.

8.2 RECOMMENDATIONS

- Although some preliminary studies are carried out for competitive adsorption of heavy metals in this work, a detailed study should be carried to explore the treatment of wastes containing number of heavy metal species, as these metals preferentially adsorbed in multi-cationic solution.
- Costing of adsorption based industrial scale treatment system be carried out to popularize the adsorption technique with carbon slurry.
- Carbon slurry has shown an excellent adsorptive characteristics for the removal of heavy metals and COD from different waste water samples.
- Carbon slurry can be used as a suitable for the treatment of industrial waste water.

REFERENCES

1. Agrawal, N. K., "Decolourization of Pulp and Paper Mill Effluent : Removal of Dyes", M.E. Thesis, University of Roorkee, Roorkee, India, 2000.

2. Allen, S. J., McKay, G. and Khudev, K. Y. H., "Intra-particle diffusion of basic dye during adsorption onto sphagnum peat", Environ. Pollut., 56, 39-50, 1989.

3. Austen G. T., " Shreve's Chemical Process Industries", Plastic Industries, 649-651, fifth edition,McGraw Hill Company Limited, Singapore,

4. Bailey S.E., Olin T. J., Bricka R. M. and Adrian D., "A review of potentially low cost sorbents for heavy metals", Water Res., Vol. 33, No. 11, 2469-2479, 1999.

5. Chauhan , S. K., Padh, M.R. and Charandas, V., "Utilization of wastes from Fertilizers Group Of Plants at G.S.F.C.", Chem. Age India, 27 (12),1023-1033, 1976

6. Das N. C., and Bandhopadhyay M., "Removal of nickel by a low cost natural medium", Indian Journal of Technology, 31,pp. 118-120, 1993.

7. David. H. F. Liu, Liptak B.G., "Environmental Engineers Handbook", Second Edition, Lewis Publishers, 1997.

8. Foust, S. D. and Alay, O. M., "Adsorption Processes for Water Treatment", Butterworths, 1986.

9. Gajghate D. G. and Reddy P.J., " COD BOD relationship for industria' wastes", IJEP, 9, 11, 805-807, 1989.

10. Gangsun and XiangJing Xu, "Sunflower Stalks as adsorbents for colour removal from textile waste water", Ind. Eng. Chem. Res., 36, 802-812, 1997.

11. Gomez-serrano V., Macias-Garcia A., Espinosa-Mansilla A., and Valenzuela-calaharro C., " Adsorption of mercury, cadmium and lead from aqueous solution on heat treated and sulphurized activated carbon", Water Research 32, 1, 1-4, 1998.

12. Gupta , V.K., Srivastava, S.K., Tyagi R., " Design parameter for the treatment of phenolic wastes by carbon columns (obtained from,fertilizer waste material", Water Res. 34, 5, 1543-1550, 2000.

13. IS: 1350 (Part-I)-1984, " Methods of tests for coal and coke (proximate analysis) ", Bereau of India Standards, Manak Bhawan, New Delhi, India.

14. Jain V.K., "Effluent treatment of nitrogenous fertilizer plant- An appraisal of biotechnological methods", Proc. Seminar on fertlizer Industry- processes problems and perspectives, Vol. II, B.H.U. Varansi, 159-168, 1988.

15. Jashni A.K. and Narbaitz R.M.," Impact of pH on the adsorption and desorption of kinetics of 2-nitro-phenol on activated carbons", Water res. 31,3039-3044, 1997.

16. Karia,V. K., "Pollution abatement at G N F C-An approach to zero effluent.", Fertiliser News, August 1983.

17. Khanna, P. and Malhotra, S. K., "Kinetics and Mechanism of Phenol Adsorption on Fly ash", Ind. J. Environ. Health, 19, 224-237, 1997.

18. Koli A., Sharma V., Sharma S. C., and Sharma S.C., " preliminary studies on the adsorption behaviour of chromium on fly ash", Chemical Engineering world, xxxii, 1,1997.

19. Lopez-delgado A., Perez C. and Lopez F. A., "Sorption of Heavy metals on blast Furnace Sludge", Water Research, 32, 4, 989-996, 1998.

20. Mahadeva Swamy M., "Studies on the treatment of phenolic waste waters using adsorption and immobilized whole cells", Ph.D. Thesis, University of Roorkee, Roorkee, India, April 1998.

21. Mahajan S. P., "Pollution and its measurement", Miscellaneous Process Industries, Tata McGraw-Hill publishing company limited, New Delhi, 258-260,1985.

22. Mall, I. D. and Prasad, J., "Pyrolysed Bagssae Char- A Low Cost Effective Effluent System for pulp and paper mill", IPPTA, 10, 2, 1998.

23. Mall, I. D., Mishra, N., Mishra, I. M., "Removal of organic matters from sugar mill effluent using bagasse fly ash and activated carbon", Research and Industry, 39, 115-119, 1994.

24. Mall, I.D., Mishra, N. & Mishra I.M., Removal of COD from Sugar Mill effluents using bagassae fly ash, Proceedings of Ninth national convention of chemical engineering and international symposium on importance of biotechnology, JUNE 5-7,1993,Institution of engineers of India, Visakhapatnam,p-402.

25. Mall, I. D., Singh, D., Singh A. K., Mishra I. M., "Detoxification of bleach plant effluent using low cost adsorbents : removal of 2,4 dichlorophenol", IPPTA, 13, 4, 11-17, 2001.

26. Mall, I. D., Tyagi S. K., "Bagasse fly ash – A low cost adsorbent for treatment of chlorophenol bearing waste water", International Conf. on Environmental Strategies for 21st Century held at Singapore, April 8-10, 1998.

27. Mall, I. D., Upadhyay, S. N. and Sharma, Y. C., "A review on economical treatment of waste waters and effluents by adsorption", Intern. J. Environ. Studies, Vol. 51, 77-124, 1996.

28. Mattson J.S. and Mark H.B. "Activated Carbon: Surface Chemistry and Adsorption From Aqueous Solution. Marcel Dekker", New York,1971.

29. Mattson, J.S.,Mark, H.B.Jr., Malbin, M.D., Weber, W.J. and Crittenden J.C., "Surface chemistry of activated carbon: Specific adsorption of phenols", J.Colloid,Inst. Sci. 31, 116, 1969.

30. Metcalf & Eddy, "Waste Water Engineering Treatment", Disposal, Reuse. 3rd edition, Tata Mc-Graw Hill, 400-402, 1991.

31. Mehrotra R., and Dwivedi N. N., "Removal of chromium from water using unconventional materials", Indian Water Works Association, Oct.-Dec.,1988.

32. Muthukumar G., Subrahmanyam P.V.R., and Sundarsan B.B., "Pollution Control in fertilizer Industry-A approach towards an Ideal solution" fertilizer news, June, 1982.

33. Nag A., Gupta N., and Biswas M. N.," Removal of chromium (VI) and Arsenic (III) by Chemically Treated Saw Dust", IJEP 19 (1): 25-29,1999.

34. Oberoi, C.K., "Adsorption of cationic pesticides from aqueous solution by clays", IJEP 10(2), 126-130,1990

35. Randall J.M., Garett V. and Bermann P.L., "Use of bark to remove heavy metal ions for waste water", Fresh products JI 24, 80-84,1974.

36. Rao, B. V. and Sastry, C.S., "Removal of dyes from waste and waste water by adsorption", I.I.T Madras,Dept. of Chemical Engg. IJEP(5), 363-373, 1987.

37. Sekhar D. and Murthy D.V.S., "Colour removal of distillery spent wash by adsorption technique", Indian Chemical Engineering Section A, 40, 4, Oct-Dec 1998.

38. Sharma D. C., and Forster C. F., " Removal of hexavalent chromium using sphagnum moss peat", Water Research, vol. 27, 7, 1201-1208, 1993.

39. Singh., A. K., Singh D. P., Pandey, K. K. and Singh, V. N., "Wallastonite as adsorbent for removal of Fe(II) from water", J. Chem. Tech. Biotechnol., 42, 39-49, 1988.

40. Singh D. K. and Mishra A., " Removal of phenolic compounds from water by using chemically treated sawdust", Indian J. Environ. Hlth., 32, 4, 345-351, 1990.

41. Singh V. K., and Tiwari P. N., "Removal and recovery of chromium (VI) from industrial wastewater", J. Chem. Tech. Biotechnolo, 69, 376-382, 1997.

42. Snell-Ettre, "Encyclopedia of Industrial Chemical Analysis", 17, 424-439, 1969.

43. Srivastava S.K. and Pant N., "Studies on the conversion of local fertilizer waste slurry into a low cost carbonaceous adsorbent" , CEW. XXI, 10, 54-56, 1986.

44. Srivastava S.K. Pant N. and Pal N., "Studies on the efficiency of a local fertilizer waste as a low cost adsorbent", Water Res. 21. 1389-1394, 1987.

45. Srivastava S.K. and Tyagi R., "Kinetic parameters for removal of substituted phenols using low carbonaceous adsorbent phenols using low cost carbonaceous adsorbent", Chem. Eng. World 24, 57-59, 1989.

43. Srivastava S. K. and Tyagi R.," Competitive adsorption of substituted phenols by activated carbon developed from the fertilizer waste slurry", Water Res.29. 483-488,1995.

46. Srivastava S.K. Tyagi R. and Pant N., "Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants", Water Res. 23, 1161-1165, 1989.

44. Traegner U. and Suidan M., "Evaluation of surface and film diffusion coefficients for carbon adsorption". Water Research, 23(3), 267-273, 1989.

45. Tutem E., Apak R. and Cagatay F. U., "Adsorptive removal of chrolophenols from water by bituminous shale", Water Res., 32, 8, 2315-2324, 1998.

46. Vaishya R. C., and Prasad S.C., " Adsorption of copper (II) on sawdust", IJEP 11 (4): 284-289,1991.

47. Venkata, G., Kumar A., "Decolorisation of pulp and paper mill effluent", M.E. Dissertation, University of Roorkee, Roorkee, India, 2001.

48. Weber W.J.Jr, and Morris, J. C., "Kinetics of adsorption on carbon from solution", J. Sanit, Engg. Div,. ASCE, 89,31,1963.

49. Weber W.J., Snoeyink V.L. and Mark H.B., "Sorption of phenol and p-nitrophenol by active carbon", Envir. Sci. Technol, 3, 198-212,1969.

50. Zogorski J.S., Faust S.D. and Hass J.H., "The kinetics of phenol by granular activated Carbon", J. Colloid Interface Sci, 55, 329-341,1976.

APPENDIX – A

Table A – 1 : Calibration curve for Chromium (VI)

Sr. No.	Concentration (ppm)	Absorbance
1	1	0.2215
2	2	0.4403
3	3	0.6261
4	4	0.9411
5	5	1.1257
6	6	1.2018
7	7	1.4316
8	8	1.5091
9	9	1.6701
10	10	1.8853
11	11	2.0145
12	12	2.1655
13	13	2.3465
14	14	2.5143
15	15	2.6504

Table A – 2 : Effect of adsorbent dose on removal of Cr (VI)

Sr. No.	Adsorbent Dose (g)	% removal
1	0.1	46.5
2	0.2	49.0
3	0.3	55.0
4	0.4	72.6
5	0.5	86.5
6	0.6	90.4
7	0.7	91.3

Table A - 3 : Effect of contact time for removal of Cr(VI) for different concentration using CS (1.0 g)

Sr. No.	Contact time (min)	C_1 = 5 ppm		C_2 = 10 ppm		C_3 = 15 ppm	
		% removal	Amount adsorbed/ amount of adsorbent (mg/g)	% removal	Amount adsorbed/ amount of adsorbent (mg/g)	% removal	Amount adsorbed / amount of adsorbent (mg/g)
1	15	58.37	0.146	32.47	0.162	11.25	0.084
2	30	65.53	0.164	34.22	0.171	13.91	0.104
3	60	72.52	0.181	41.09	0.205	30.50	0.228
4	120	79.26	0.198	59.40	0.296	47.60	0.357
5	180	82.87	0.207	75.13	0.376	70.39	0.528
6	240	87.16	0.218	86.10	0.435	85.05	0.638
7	300	91.78	0.226	90.35	0.452	89.85	0.674
8	360	91.96	0.227	91.09	0.455	90.79	0.681

Table A – 4 : Effect of initial concentration on removal of Cr (VI) Using CS (1.0 g)

Sr. No.	Initial Concentration (ppm)	% removal	Amount adsorbed/ Amount of adsorbent (mg/g)
1	5	91.96	0.2270
2	10	91.43	0.4571
3	15	91.09	0.6831
4	25	89.79	1.1224
5	30	87.08	1.3062
6	40	85.41	1.7082
7	50	76.44	1.9110

Table A – 5 : Lagergren Plot for removal of Cr (VI)

Sr. No.	Time (min)	Log (q_e-q)
1	15	-0.491
2	30	-0.504
3	60	-0.517
4	120	-0.747
5	180	-1.004
6	240	-1.398
7	300	-1.721

Table A – 6 : Freundlich Isotherm for adsorption of Cr (VI)

Sr. No.	Initial Concentration (ppm)	Log C_e	Log q_e
1	5	-0.3958	-0.6440
2	10	-0.0670	-0.3399
3	15	0.1260	-0.1655
4	25	0.4070	0.0501
5	30	0.5884	0.1160
6	40	0.7661	0.2325
7	50	1.0711	0.2813

Table A – 7 : Langmuir Isotherm for adsorption of Cr (VI)

Sr. No.	Initial Concentration (ppm)	$1/C_e$	$1/q_e$
1	5	2.4875	4.4052
2	10	1.6686	2.1877
3	15	0.7482	1.4639
4	25	0.3918	0.8909
5	30	0.2579	0.7655
6	40	0.1713	0.5854
7	50	0.0849	0.5233

Table A – 8 : Weber-Morris intra-particle diffusion plot for removal of Cr (VI)

Sr. No.	Time (min)	$Time^{1/2}$ $(min)^{1/2}$	Amount of Cr (VI) adsorbed per unit weight of adsorbent (mg/g)
1	15	3.87	0.1515
2	30	5.48	0.1623
3	60	7.46	0.1711
4	120	10.95	0.2970
5	180	13.42	0.3756
6	240	15.49	0.4305
7	300	17.32	0.4567

Table A - 9 : Calibration for removal of Ni (II) using AAS

Sr. No.	Concentration (ppm)	Mean absorbance
1	2	0.1174
2	4	0.1802
3	6	0.2376

Table A – 10: Effect of contact time on removal of Ni (II)[10ppm] using CS (1.0g)

Sr. No.	Contact time (min)	% removal
1	15	74.83
2	30	77.23
3	60	79.84
4	120	84.02
5	180	88.76
6	240	90.26
7	300	90.29

Table A – 11: Effect of initial concentration on removal of Ni (II) using CS (1.0g)

Sr. No.	Initial concentration (ppm)	Final concentration (ppm)	% removal
1	10	1.319	86.81
2	20	6.633	66.83
3	25	10.962	56.15
4	30	14.847	50.51
5	40	21.861	45.34

Table A - 12 : Lagergren plot for removal of Ni (II)

Sr. No.	Contact time (min)	Log (q_e-q)
1	15	-0.955
2	30	-1.025
3	60	-1.097
4	120	-1.162
5	180	-1.212
6	240	-1.503

Table A – 13 : Freundlich Isotherm for adsorption of Ni (II)

Sr. No.	Initial Concentration (ppm)	Log C_e	Log q_e
1	10	0.1202	-0.363
2	20	0.8217	-0.175
3	25	1.0398	-0.153
4	30	1.1716	-0..121
5	40	1.3390	-0.042

Table A – 14: Langmuir Isotherm for adsorption of Ni (II)

Sr. No.	Initial Concentration (ppm)	$1/C_e$	$1/q_e$
1	10	0.758	2.304
2	20	0.151	1.497
3	25	0.091	1.424
4	30	0.057	1.324
5	40	0.045	1.103

Table A – 15 : Weber-Morris intra particle diffusion plot for removal of Ni (II)

Sr. No.	Time (min)	$\text{Time}^{1/2}$ $(\text{min})^{1/2}$	Amount of Ni (II) adsorbed per unit weight of adsorbent (mg/g)
1	15	3.87	6.98
2	30	5.48	7.15
3	60	7.46	7.26
4	120	10.95	7.43
5	180	13.42	7.51
6	240	15.49	8.01

Table A - 16 : Calibration for removal of Zn (II) using AAS

Sr. No.	Concentration (ppm)	Mean absorbance
1	0.5	0.0928
2	1.0	0.1940
3	1.5	0.2757

Table A - 17: Effect of contact time on removal of Zn (II) [10ppm] using CS (1.0 g)

Sr. No.	Contact time (min)	% removal
1	15	64.5
2	30	73.0
3	60	74.0
4	120	83.0
5	180	88.5
6	240	93.5
7	300	93.7

Table A-18: effect if initial concentration on removal of Zn (II) using CS (1.0g)

Sr. No.	Initial concentration (ppm)	Final concentration (ppm)	% removal	mg Zn(II)/ g of CS
1	10	0.62	93.78	0.469
2	20	4.40	78.00	0.780
3	25	6.03	75.88	0.948
4	30	8.32	72.26	1.084
5	40	11.85	70.38	1.407
6	50	18.65	62.71	1.567

Table A - 19: Lagergren plot for removal of Zn (II)

Sr. No.	Contact time (min)	Log (q_e-q)
1	15	-0.9550
2	30	-1.0250
3	60	-1.0974
4	120	-1.1647
5	180	-1.2118
6	240	-1.5030
7	300	-2.0315

Table A – 20 : Freundlich Isotherm for adsorption of Ni (II)

Sr. No.	Initial Concentration (ppm)	Log C_e	Log q_e
1	20	0.6434	-0.1079
2	25	0.8007	-0.0229
3	30	0.9201	0.0350
4	40	1.0737	0.1484
5	50	1.2705	0.1952

Table A – 21 : Langmuir Isotherm for adsorption of Zn (II)

Sr. No.	Initial Concentration (ppm)	$1/C_e$	$1/q_e$
1	10	1.6077	2.1326
2	20	0.2272	1.2820
3	25	0.1658	1.0543
4	30	0.1202	0.9225
5	40	0.0844	0.7105
6	50	0.0536	0.6379

Table A – 22 : Weber-Morris intra particle diffusion plot for removal of Zn (II)

Sr. No.	Time (min)	$Time^{1/2}$ $(min)^{1/2}$	Amount of Ni (II) adsorbed per unit weight of adsorbent (mg/g)
1	15	3.87	0.3225
2	30	5.48	0.3650
3	60	7.46	0.3700
4	120	10.95	0.4150
5	180	13.42	0.4425
6	240	15.49	0.4575
7	300	17.32	0.4685

Table A - 23: Correlation coefficient (r) for fitting experimental data to straight line for Lagergren plot, freundlich isotherm, Langmuir isotherm and Weber-Morris intra particle diffusion plot

Adsorbent	Adsorbate	Correlation Coefficient			
		Lagergren plot	Freundlich isotherm	Langmuir isotherm	Weber & Morris plot
Carbon slurry	Cr (VI)	0.951	0.99	0.9538	0.9712
	Ni (II)	0.9076	0.9783	0.9499	0.8937
	Zn (II)	0.9076	0.9753	0.9889	0.9712

Table A – 24 : Calibration for determination of phenol

S. No.	Concentration (ppm)	Absorbance
1	1	0.125
2	2	0.230
3	3	0.350
4	4	0.500
5	5	0.600

Table A-25: Freundlich Isotherm for removal of COD from Phenol- formaldehyde resin plant effluent

Sr. No.	Log qe	Log ce
1	-0.5185	5.1103
2	-0.5199	5.0083
3	-0.5302	4.8756
4	-0.5316	4.6822
5	-0.5346	4.3251
6	-0.5767	3.7396
7	-0.8013	3.4544
8	-1.3767	2.6580

Table A-26: Langmuir Isotherm for removal of COD from Phenol- formaldehyde resin plant effluent

Sr. No.	1/qe	1/ce
1	3.300	7.756×10^{-6}
2	3.311	9.808×10^{-6}
3	3.330	13.316×10^{-6}
4	3.401	20.786×10^{-6}
5	3.425	47.301×10^{-6}
6	3.773	182.126×10^{-6}
7	6.329	351.185×10^{-6}
8	23.809	2197×10^{-6}